THE FORMATION AND THERMAL STABILITY

OF

POLYVINYL CHLORIDE

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by

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SUMMARY

The thermal stability of Polyvinyl chloride (PVC) was studied. Three phases of degradation were investigated,

1. Dehydrochlorination
2. Discolouration
3. Cross linking

The effect of the polymerisation reaction on the final stability of the polymer was also studied, by varying,

1. The type and concentration of initiator
2. The polymerisation temperature
3. The percent polymer conversion
4. The method of polymerisation

The polymers thus formed were characterised and then degraded. The results indicate an increase in stability with decrease in polymerisation temperature.

The change in initiator type and concentration altered the kinetics of the polymerisation reaction and hence the properties of the polymer formed.

Polymers obtained at different conversions exhibited a stability 'maxima' around 40-60% conversion.

Some of the polymers prepared in solution showed marked increase in stability and those prepared by photo irradiation showed a different mechanism of degradation. Two commercial polymers were also studied for comparison.

The activation energy for the dehydrochlorination of PVC in solution was found to be 21 k cal/mole and the reaction showed 3 distinct stages.

The discolouration, or the polyene formation in PVC due to thermal degradation was characterised into two different reactions with different activation energies.

The changes in molecular weight during the degradation is reported. There exists an inverse relationship between the molecular weight of the polymer and the rate of dehydrochlorination.

TABLE OF CONTENTS

Page

CHAPTER 4 : THERMAL STABILITY OF PVC

CHAPTER 1

INTRODUCTION

INTRODUCTION OF POLYVINYL CHLORIDE (PVC)

The preparation of vinyl chloride by Regnault in 1835[1-2] was the initial step in the process which led to the first accidental observation of PVC in 1872 by Baumann.[3]

In 1912 Ostromislensky patented a polymerisation process for PVC in Moscow; a new method of vinyl chloride preparation from acetylene and HCl was also developed in the same year by F. Klatte.

It was not until 1928 that the problem of processing PVC resin was solved. The high softening point (and its closeness to its decomposition temperature) and bad flow properties were the major stumbling blocks. Vinyl chloride copolymers and the use of plasticisers provided possible answers to these difficulties. The decisive point in PVC technology was the breakaway from rubber processing ideas and accepting that a high temperature ($160^{o}C$) was needed for PVC processing as reported by Dr. Wisch's in 1937.

In Britain initially two methods of preparation of PVC were used. The first was the acetylene (by ICI) in 1937 and was followed a few years later by the ethylene dichloride process (Distillers Co.).

1940 saw the introduction of the emulsion polymerisation process on a large scale. From this small beginning, 85 tons/year in 1940, PVC world production has grown to more than 4 million tons/year.

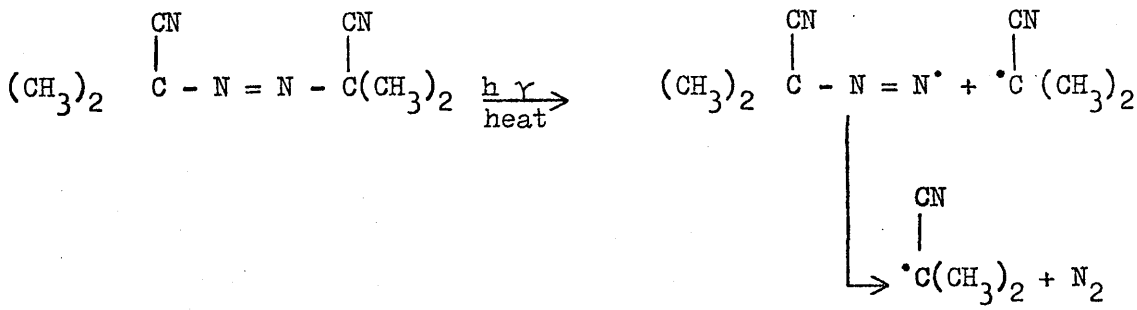
POLYMERISATION

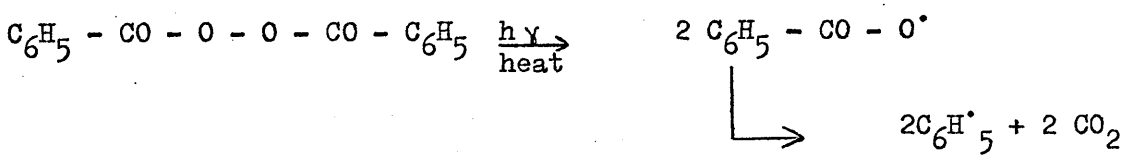
Mechanism of Vinyl Polymerisation:

The addition polymerisation of vinyl monomers of the type

$CH_2 = CHX$ such as styrene and vinyl chloride was known long before Staudinger[4], who, in 1920, proposed chain structures for polystyrene and polyoxymethylene. He also suggested a mechanism for polymerisation which involved free radical intermediates. In 1927, Taylor and Bates[5] produced the first complete free radical mechanism for a polymerisation reaction. This was further confirmed by detailed kinetic analysis. It is now generally accepted that there are four main reactions involved; initiation, propagation, chain transfer and termination.

Initiation : This is accomplished by irradiating or heating a solution of monomer containing a free radical initiator in most cases. In this work 2' - azo-bis-isobutyronitrile and benzoyl peroxide were mainly used: these liberate free radicals through the following mechanism respectively :





and can be represented thus :

$$\text{Initiator} \longrightarrow 2R_c^{\bullet}$$

The radical, $R_c^{\bullet}$, then adds to the double bond of a vinyl monomer molecule

$$R_c^{\bullet} + CH_2 = CHX \longrightarrow R_c - CH_2 - {}^{\bullet}CHX$$

where X represents substituent atoms or groups according to the monomer being considered, in this case being Cl.

Propagation : The polymer chain is built up by a series of reactions in which monomer molecules successively add to the free radical produced in the initiation step.

$$R_c - CH_2 - {}^{\bullet}CHX + CH_2 = CHX \longrightarrow R_c - CH_2 - CHX - CH_2 - {}^{\bullet}CHX$$

$$R_c - (CH_2 - CHX)_n - CH_2 - {}^{\bullet}CHX + CH_2 = CHX \longrightarrow$$

$$R_c - (CH_2 - CHX)_{n+1} - CH_2 - {}^{\bullet}CHX$$

Chain Transfer : This occurs when the propagating radicals react with solvent, monomer, initiator or polymer molecules to form polymer. In this case, the free radical is not removed from the system but is transferred to start another polymer chain thus limiting the length of the polymer sequence in general,

$$R_c - (CH_2 - CHX)_n - CH_2 - {}^{\bullet}CHX + R^1H \longrightarrow$$

$$R_c - (CH_2 - CHX)_n - CH_2 - CHHX + {}^{\bullet}R^1$$

R^1H represents any chain transfer agent, ${}^{\bullet}R^1$ is the radical derived from it.

In the specific case of chain transfer with monomer, the following applies :

$$\sim\sim CH_2 - {}^{\bullet}CHX + CH_2 = CHX \begin{cases} \longrightarrow \sim\sim CH = CHX + CH_3\ {}^{\bullet}CHX \\ \text{or} \\ \longrightarrow \sim\sim CH_2 - CH_2X + CH_2 = {}^{\bullet}CHX \end{cases}$$

In the case of chain transfer with polymer, we have

$$\sim\sim CH_2 - CHCl \sim\sim + \sim\sim CH_2 - {}^{\bullet}CHX$$

$$\sim\sim\sim CH_2 - \underset{\bullet}{\overset{X}{C}} \sim\sim\sim \quad \text{or} \quad \sim\sim\sim CH - \underset{\bullet}{CHX} \sim\sim\sim$$

$$+ \sim\sim CH_2 - CH_2X$$

Termination : Takes place when two of the radicals produced in the propagation step react with each other either by combination :

$$R_c - (CH_2 - CHX)_m - CH_2 - \dot{C}HX + R_c - (CH_2 - CHX)_n - CH_2 - \dot{C}HX \longrightarrow$$

$$R_c\ (CH_2 - CHX)_m - CH_2 - CHX - CHX - CH_2 - (CHX - CH_2)_n - R_c$$

or by disproportionation :

$$R_c - (CH_2 - CHX)_m - CH_2 - \dot{C}HX + R_c - (CH_2 - CHX)_n - CH_2 - \dot{C}HX \longrightarrow$$

$$R_c - (CH_2 - CHX)_m - CH = CHX + R_c - (CH_2 - CHX)_n - CH_2 - CH_2X$$

kinetically the two reactions are similar in that both involve the removal of two radicals. Radioactive tracer techniques using C^{14} have shown that in most monomers studied 'combination' is the preferred reaction especially at low temperatures. Termination can also occur by interaction of the radicals with initiator fragments, impurities (such as oxygen), or inhibitors. Where this occurs to any great extent the kinetic analysis of the system is affected markedly.

Kinetics of Vinyl Polymerisation :

In formulating a kinetic scheme three assumptions are made :

1) The reactivity of the radical growing chain is independent of the radical chain length, thus one single velocity coefficient can be used for each of the polymerisation steps.

2) The major portion of the monomer is removed in the propagation step. The rate of polymerisation is therefore equal to the rate of monomer removal in this step.

3) A steady state concentration of radicals is rapidly attained. The rate of termination is therefore equal to the rate of initiation.

A kinetic scheme can then be formulated according to

	Rate	
Initiation		
$\text{Initiator} \longrightarrow 2\,R_c^{\bullet}$	$2k_d\,[\text{Initiator}]$	-------- 1.1
$R_c^{\bullet} + M \longrightarrow R_1^{\bullet}$	$k_I\,[R_c^{\bullet}]\,[M]$	-------- 1.2
Propagation		
$R_1^{\bullet} + M \longrightarrow R_2^{\bullet}$		
$R_n^{\bullet} + M \longrightarrow R_n^{\bullet} + 1$	$k_p\,[R^{\bullet}]\,[M]$	-------- 1.3
Chain Transfer		
$R_n^{\bullet} + M \longrightarrow P_n + M^{\bullet}$	$k_{tr}\,[R^{\bullet}]\,[M]$	-------- 1.4
Termination		
$R^{\bullet} + R^{\bullet} \longrightarrow$ Polymer	$k_t\,[R^{\bullet}]^2$	-------- 1.5

Where $R_c^{\bullet}$ represents a radical derived from the initiator

M represents a monomer molecule

$R_n^{\bullet}$ represents a growing polymer radical of n, monomer units

$M^{\bullet}$ represents a radical from the monomer derived by hydrogen atom transfer.

k_d is the rate constant for the initiator decomposition

k_I is the rate constant for the radicals derived from the initiator and the monomer M.

k_p, k_{tr}, k_t are the rate constants for propagation, chain transfer and termination respectively.

When the steady state has been attained, then the rate

$$d[R^{\bullet}]/dt = I - k_t\,[R^{\bullet}]_s^2 \qquad \text{-------- 1.6}$$

where $\left[R^{\bullet}\right]_s = \left(\frac{I}{k_t}\right)^{0.5}$ -------- 1.7

and $\frac{-dM}{dt} = k_p \left(\frac{I}{kt}\right)^{0.5} . \left[M\right]$ -------- 1.8

Polymerisation of Vinyl Chloride:

Autocatalysis, the polymerisation of vinyl chloride is a heterogeneous process as the polymer produced is insoluble in the monomer. Pratt[6] showed that the free radical polymerisation of vinyl chloride exhibits an autocatalytic effect in the temperature range 25 - 96°C. This is in complete contrast to homogeneous systems in which the rate of polymerisation gradually decreases with conversion due to the consumption of monomer. The bulk polymerisation of vinyl chloride has been extensively studied and detailed kinetic studies have shown that autoacceleration occurs in the early stages of polymerisation[7-10]. Bengough and Norrish[11] accounted for this by suggesting that bimolecular termination is more difficult due to the formation of mobile radicals by chain transfer reactions with polymer.

They also indicated that transfer to monomer is important and occurs readily since the molecular weight of polymers is nearly independent of the catalyst concentration. Nevertheless, it would not be expected that radicals of very long life would arise in this way since the ready transfer to monomer would destroy surface immobilised radicals.

Magat[12] treated the initial acceleration as a long pre-effect arising from an abnormally low termination coefficient.

Effect of Oxygen, Oxygen is a powerful inhibitor and Pratt[6] found that the longer induction periods were followed by the higher rates of reaction, showing that during inhibition a labile peroxide is formed by direct reaction between the monomer and oxygen. Work performed by Garton

and George[13] indicated the presence of carbonyl group and a lowering in molecular weight for PVC which was polymerised under traces of oxygen.

Effect of Conversion on Reaction, Breitenbach and Schindler[9] fitted their results for vinyl chloride polymerisation at 50°C with a benzoyl peroxide concentration of 10^{-1} mole % by the empirical equation,

$$\% \text{ polymerisation} = 1.94\ t + 0.0223\ t^2$$

where t is the reaction time in hours. Arlman and Wagner[14] obtained similar results.

Homogeneity

Solution polymerisation does not manifest any acceleration nor does added polymer have any catalytic influence[15]. In the presence of carbon tetrabromide[16,17] as a transfer agent the rate is constant and has approximately the maximum value which would be obtained in the absence of the additive. This was explained by assuming that in the absence of a transfer agent vinyl radicals through transfer to monomer are formed which were considered relatively stable and hence result in self-retardation. This overlooks the fact that transfer with monomer and with CBr_4 are independent and not competitive.

In this work most of the polymers prepared were bulk polymers covering a temp. range of - 75°C to + 140°C utilising both benzoyl peroxide and 1 : 1 azobisisobutyronitrile as initiators in concentrations of 0.01, 0.10 and 1.0 moles %

Solution, thermal polymerisation of vinyl chloride in various liquids of differing degree of solubility at 60°C were also conducted in our study to determine the effect of heterogeneity

and of chain transfer with solvent reactions on the thermal stability of the polymer.

Also both commercial emulsion and suspension polymers were briefly investigated.

STRUCTURE

Chemical Composition : The basic repeating unit of polyvinyl chloride chain is (- CH_2 - CHCl -) in the ratio of C24 : H3 : Cl 35.5 or about 38% : 5%:57% respectively with a molecular weight of 62.5

The monomer vinyl chloride contains two functional groups the chloride group and the double bond. The Cl atom conformatory with all such halogen atoms attached to a double bonded carbon, is quite unreactive. This inert character is so pronounced that vinyl chloride will not react with magnesium to form a Grignard reagent. The reactions of the double bond, are much more varied and numerous.

Molecular Chain Length : In most commercial resins, chains contain between 500 and 2000 units, giving a number average molecular weight of 30,000 to 100,000, polymerisation temperatures play a critical role in determining the chain length.

Molecular Chain Order : PVC was demonstrated to have a regular "head-to-tail" arrangement by Marvel et al[18-20].

$\sim\sim\sim CH_2$ - CHCl - CH_2 - CHCl - CH_2 - CHCl

The polar nature of the double bond ($CH_2 = \overset{+}{C}H \longrightarrow \overset{-}{C}l$) is perhaps responsible for this arrangement. Flory[21] further confirmed this by theoretically determining that the residual chlorine content after the Zn dust induced degradation is about 13.53% in the case of a regular structure, which coincides with the experimentally found value of between 13 and 16%.

Branching : The presence of tertiary chlorides in PVC and hence chain branching was first estimated at 20 per molecule by Cotman[22] by using reductive hydrogenation techniques.

Similar studies were performed by Krasovec[23]. These branches are probably formed by chain transfer between a growing radical and an already formed polymer molecule as discussed earlier, or by back-biting. The work of Kharasch et al[24] with diacetyl peroxide and various chloro-alkanes indicated that chain transfer reaction is most likely to take place with the hydrogen on the same carbon as chlorine. This evidence led Baum and Wartman[25] to believe that most of the branches in PVC are attached to the chain in a tertiary chloride type structure. The amount of branching is thought to increase with increasing temperature of polymerisation[26]. Freeman and Manning[27] have shown a relation between increasing molecular weight and an increase in chain branching. Branching at 90% conversion is about 10 times the branching at 10% which amounted to 15 branches or an involvement of only 1% of the monomer at that low conversion.

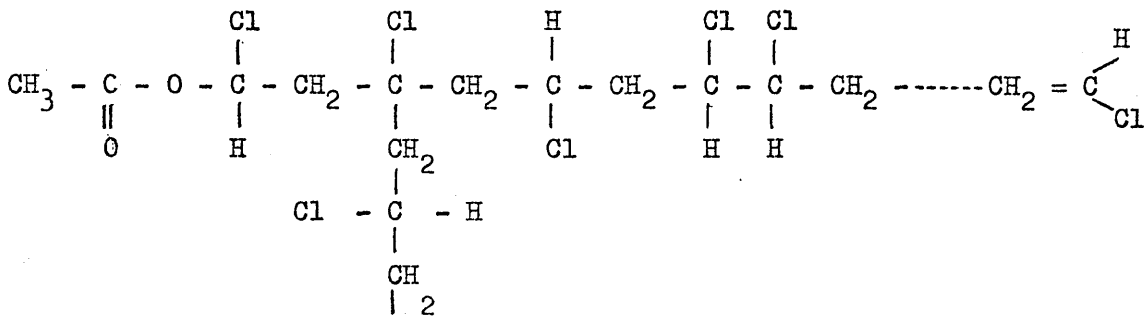
Crystallinity and Stereoregularity : PVC chains are mostly atactic[70]. If crystallinity does occur, it is mainly a syndiotactic structure and does not exceed 10 to 15%. Through specific polymerisation conditions, especially low temperature, crystallinity can be enhanced[28-30].

Unsaturation: Carbon - carbon double bonds at the chain ends or terminal saturation can also manifest itself. These may be formed either by chain transfer reaction or from termination by disproportionation. The former is believed to be the main cause[11] and results in a β - chloro unsaturated structure,

$$\sim\sim\sim CH_2\ CHCl^{\bullet} + CH_2 = CHCl \longrightarrow \sim\sim CH = CHCl + CH_3\ {}^{\bullet}CHCl$$

Extraneous Groups : Other variations from ideality could be introduced through the incorporation of extraneous groups, mainly at the chain ends. The origin of such groups could be from : solvents, chain transfer agents, initiator fragments, oxidation of the polymer or initiator fragments, during polymerisation, and by possible post oxidation of the polymer.

Disorder Limit : The following structure represents a PVC model molecule containing most of the irregular structures mentioned in the above paragraphs.



It is not intended to suggest that a single molecule having all these features is likely to exist.

Degradation and Stability of Polymers : Polymer degradation reactions have aroused interest for as long as polymeric materials have been used commercially. Papers were published more than 100 years ago[31,32] on the degradation of rubber and gutta percha. The systematic study of polymer degradation reactions, only started about 1930 with the birth of the modern plastic industry. Real progress in understanding polymer degradation began to be made in the period 1950-1955 as reflected by the upsurge of monographs. This was mainly due to (a) new methods which were developed to follow accurately the loss in weight and the rate of production of volatile material and their

analytical identification (b) methods of molecular weight measurement, especially viscometry and osmometry were being established (c) the trial and error method of using stabilisers reached the limits of their usefulness (d) the fact that well known chemical reactions often assumed new features when occurring in a polymer chain environment. The latter created a new inquisitive excitement in the chemical circles at the same time as a new specialised breed of chemists were evolving 'the polymer chemists'. With this intensified interest the following sequence of evolutionery rationalisation took place. (i) The essential features of the simpler degradation mechanisms were established within a context of polymer chemistry. (ii) As simultaneously more understanding of polymerisation mechanisms and kinetics was achieved, efforts were made to relate polymerisation parameters to degradation phenomena (iii) with this new understanding, the advent of the plastic age, the accessibility to sophisticated analytical instrumentation and exposing materials to their limits through the evolution of the aerospace technology; efforts were diverted from the study of degradation to macromolecular stabilisation by emphasising on polymer synthesis and characterisation of new and more thermally stable species and building polymer chains around them by molecular tailoring and or rearrangement. The net outcome of this is the creation of a three tier plastic technology (a) general purpose plastics (b) engineering plastics (c) speciality (aerospace) polymers some of which have not been commercialised at all, either due to inavailability of practical manufacturing capabilities or their intractibility in existing processing equipment or due to their high cost.

The work in this thesis belongs mainly in category (ii). Within this context the main general classes by which degradation could manifest itself in most polymers are :

1 - Chain Scission Reactions

1 - 1 Depolymerisation or

1 - 2 Random Chain Scission

2 - Non Chain Scission reactions

2 - 1 Side group elimination

2 - 2 Cross linking

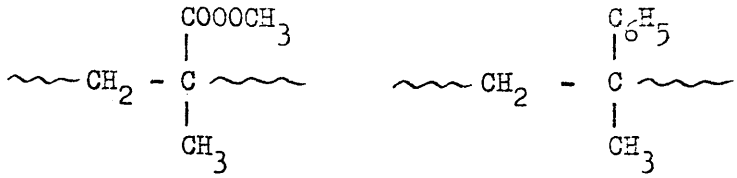
1 - Chain Scission Reactions

In this case degradation causes scission of the main polymer chain.

1-1 - Systematic Chain Scission "Depolymerisation".

This is the reverse process of polymerisation, and causes the polymer to lose successive monomer units thus the yield of monomer is relatively high.

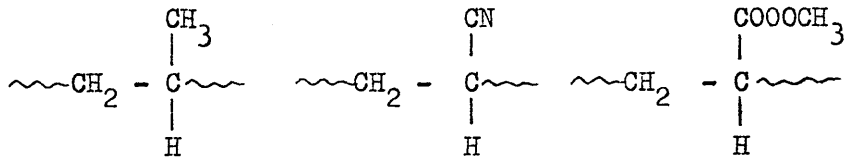
Depolymerisation is regarded as a free radical process involving initiation, depropagation and termination steps. Polymers which exhibit this type of behaviour are characterised by their low heats of polymerisation, (in the region of 10-13 k.cal mole^{-1}). Grassie[33] also suggested that the incorporation of a quaternary carbon atom in the backbone of the polymer chain assists the production of large amounts of monomer. Polymethyl methacrylate[34] and poly- - methylstyrene, undergo this type of breakdown.



Polymethyl methacrylate Polyα - methylstyrene

1 - 2 Random Chain Scission

The polymer is split in fragments which in general contain a number of monomer units. The replacement of a substituent of a quaternary carbon atom by hydrogen atom decreases the monomer yield. The heat of polymerisation of such polymers is high (about 20 k cal $mole^{-1}$). Polyolefins[35] are examples of polymers which undergo random chain scission when subjected to heat,



Polypropylene Polyacrylonitrile Polymethylacrylate

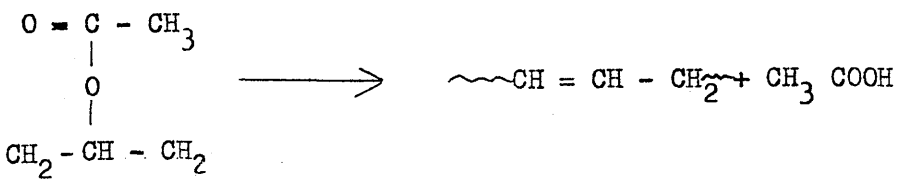
2 - Non Chain Scission reactions

In this case the polymer chain remains intact and a modification of the substituent group or groups takes place.

2 - 1 Sidegroup elimination

Polyvinyl esters degrade in this way with the evolution of the corresponding acid from the substituent ester group.

Thus, polyvinyl acetate loses acetic acid, whilst simultaneously forming a double bond in the polymer molecule.

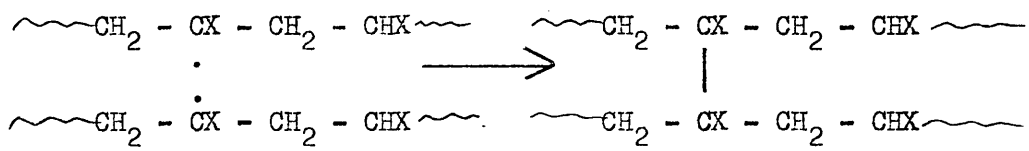


Polyvinylacetate

The features of this type of degradation are that it can take place at a much lower temperature (about 160 - 180°C) and the polymer structure itself affects the ability for the reaction to occur. Polyvinyl chloride and polyvinylidene chloride also belong in this class.

2 - Cross Linking

In the cross linking reaction, a polymer network may be obtained by the combination of polymer radicals or molecules during the course of degradation.



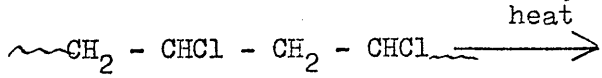
PVC also undergoes this type of degradation although the actual mechanism is not as yet well defined.

This in general is a brief outline of the various reactions, which may occur during the course of degradation.

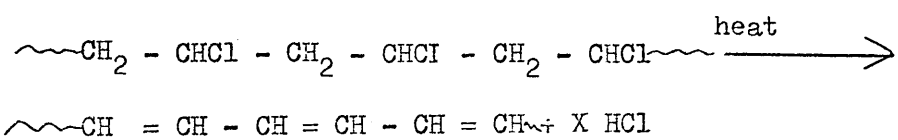
Degradations of Polyvinylchloride

Manifestations and Main Aspects of Degradation : At room temperature and in the absence of UV - light PVC is inherently stable. Increase in temperature to about 100°C leads to decomposition. Depending on its advancement, decomposition can express itself through one or all of the following sequential but overlapping phases.

1 - Dehydrochlorination ⟶ evolution of HCl



2 - Polyene Chain formation ⟶ formation of chromophores and discolouration



3 - Chain Scission $\xrightarrow{\text{heat}}$ decrease in viscosity

$$\sim CH_2 - CHCl - CH_2 - CHCl \sim \longrightarrow \sim CH_2 - {}^{\bullet}CHCl + {}^{\bullet}CH_2 - CHCl$$

4 - Cross linking $\longrightarrow$ increase in viscosity and formation of insoluble gels

$$-CH_2 - CHCl - {}^{\bullet}CH - CHCl$$

$$+$$

$$- CH_2 - CHCl - \dot{C}H - CHCl$$

$$\longrightarrow$$

$$- CH_2 - CHCl - CH - CHCl$$

$$\qquad\qquad\qquad\quad |$$

$$- CH_2 - CHCl - {}^{\bullet}CH - CHCl$$

This, of course, is accompanied by a progressive deterioration of physical properties.

Dehydrochlorination is accompanied by the introduction of double bonds, the proper concentration of the latter is responsible for the development of colour in the polymer. Dehydrochlorination is substantially complete in 30 minutes at 300°C. At these high temperatures, small amounts of aliphatic, unsaturated and aromatic hydrocarbons are formed, but free chlorine or hydrogen have not been detected[36,37]. The rate of decomposition increases rapidly with the degradation temperature.

Activation energies of dehydrochlorination have been measured under a variety of conditions and the values range from 24 - 33 k cal/mole for dry polymer in inert atmosphere with a mean value of about 29 k cal/mole ignoring the rather high value of 38.5 to 50.8 obtained under an atmosphere of helium by Bataille and Van[38]. In presence of oxygen a lower figure around 24 k cal/mole is reported. Values obtained in solution studies also tend to be lower with a mean value of around 26 k cal/mole.

Table 1-1 summarises most of the relevant quantitative studies of thermal dehydrochlorination conducted since 1960[39].

Dehydrochlorination can be considered as a precursor to the colour or polyene formation reaction.

TABLE 1 - 1

SUMMARY OF QUANTIATIVE STUDIES OF
THERMAL DEHYDROCHLORINATION OF POLYVINYL CHLORIDE

Polymer[a] Characteristics	Conditions[b] of Degradation	Sample Molecular Weights or Viscosities	Temperature Range (C)	E (k cal/mole)	Reference
L.A. B	in vacuo		235-260	26 30 32	36
C.F.	under N_2 under O_2	1.02[c] 5.1 x 10^4[e]	180-250	33 24	40
C.P.	under N_2 under O_2	6.5 x 10^4	150-190 200-250	33 24	41
L	Solution under N_2		178-212	22.8 22.8 24.0 23.3	42
C.F. L.	in vacuo		193-233	28	43
C.P.	Solution under N_2 ethyl benzoate benzyl alcohol dichloron- aphthalene dioctylphthlate tritoluyl- phosphate benzophenone	1.10[c]	178 243	 22 22 25 25 30 30	44
L.	under N_2		100-180	31.5	45
C.	under N_2		150-210	29.5	46
C.P.	Solution under N_2		160-200	30	47
C.U.	Solution under argon	7 x 10^4[g]	175-210 210-265	20.3 25.6	48
C. C.F.	TGA in air	1.002[c] 1.152 1.012 0.752 0.397	up to 400	35 17 40 35 48	49
C.U.	sealed in vacuo	1.05[c] 5.2 x 10^4[e] 13 x 10^4[f]	80-130 above 180	28 30-31	50
C.U.	TGA		up to 155	27	51

Polymer[a] Characteristics	Conditions[b] of Degradation	Sample Molecular Weights or Viscosities	Temperature Range (C)	E (k cal/mole)	Reference
C.P.	TGA N_2			23.6	52
	ESR Air			23.1	
L.(linear)	N_2			29.9	
L	Solution under N_2	1.12[c]	170 207		53
		5.1×10^4[e]			
	di-2-ethylhexyl phthalate			29.8	
	ethyl benzoate			27.8	
	tricresyl-phosphate			28.2	
	triphenyl-phosphate			28.5	
	benzophenone			28.5	
	nitrobenzene			24.0	
C	DTG	1.9×10^4[d]	up to 400	41.2	38
	DTA	3×10^4		44.0	
	TGA	3.3×10^4		50.8	
	in helium	3.5×10^4		38.5	
		4.9×10^4		47.1	

[a] A = azoisobutyrontrile initiator B = benzoyl peroxide initiator. C = commercial polymer. F = fractionated U = unpurified P = purified L = Laboratory prepared polymer. [b] DTG = differential thermogravimetric analysis. DTA = differential thermal analysis TGA = thermogravimetric analysis.

c Viscosity

d Number average obtained from gel permeation chromatography

e Number average

f Weight average

g Viscosity average

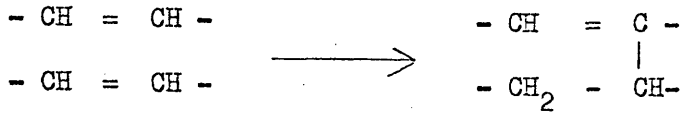
Polyene Chain formation : The colouring of the polymer results from the formation of conjugated double bonds. The intensity of this colour changes as the degradation proceeds, varying from yellow initially, to reddish brown and finally black. The formation of reddish - brown colour occurs at degrees of dehydrochlorination of as low as 0.1% at 200°C at which temperature chain scission and cross linking reactions are also likely to occur. Lewis and Calvin[54] have suggested that a 'sequence' of seven double bonds was the minimum for any colour formation. The formation of long conjugated polyene structures during the early stages of the reaction[55], particularly in linear polymers[56] is indicative of a chain reaction rather than a random process. Ozonolysis of PVC after low extents of dehydrochlorination does not cause a significant drop in molecular weight[43,57] which is further evidence for the presence of a few long polyene chains rather than the occurrence of random double bonds. There is lack of agreement concerning estimates of polyene sequence lengths[56,58-64] varying from 2 all the way to 30 double bonds depending on wavelength and the sequence distribution. Factors such as branching or the occurrence of structural irregularities could interrupt degradation chains and give rise to different values for different polymers. However simultaneous measurements of liberated hydrogen-chloride and polyene unsaturation by Braun and Thallmaier[46] showed that correlation only occurred at very low extents of reactions. With increasing degradation time a smaller polyene concentration relative to the liberated HCl was found. The sequence distribution at the same time shifts noticably towards shorter sequences probably due

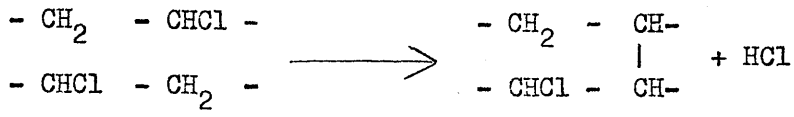
to consecutive secondary reactions leading to loss of sequence length through chain scission or cross linking. Thus there are many more molecules with 2 or 3 double bonds than with 4 or 5. As the number of double bonds increases beyond 7, the number of molecules formed decreases rapidly, and there would be very few, if any, polyene chains containing more than 30 conjugated double bonds. Further evidence of initial long polyene chains comes from ESR studies[56] comparing linear syndiotactic PVC with polymers containing either tertiary chlorine or tertiary hydrogen atoms. A kinetic chain length of the order of 10^5 was calculated which is several magnitudes higher than observed polyene sequence lengths; if this is correct then either propagating species transfers across the polymer molecules with great facility or the unspecified consecutive reactions mentioned above have an even greater role. Another suggestion[65] is that conjugated sequences with a large enough number of double bonds may become excited to the triplet state even at room temperature certainly at 170-200°C. Conversion of the polyene back into the singlet state yields energy which may excite the C-Cl bond and initiate further degradation reactions presumably cross linking. Recently efforts have been reported to kinetically study discolourations[120] as related to dehydrochlorination, the most recent study is by Ocskay and coworkers where they derived the equation

$$\frac{HCl}{I_o} = \frac{1}{\alpha k_t} \qquad Ct_\tau$$

C, being the degree of discolouration, α, a proportional factor, I_o, binding capacity of stabiliser, τ- induction period.

Chain Scission and Cross Linking. According to Imoto and Otsu[66] after two hours at 180°C, 80% of the polymer is insoluble, by separating the insoluble fraction from the soluble one, they found that the soluble fraction undergoes chain rupture, and its molecular weight drops. Cross-linking can result via the following reactions:





the initial reaction between unsaturated portions of the chain should predominate. A certain amount of HCl would be evolved with subsequently some unsaturation.

Druesedow and Gibbs[67] had previously studied the molecular weight changes under oxygen and found that the viscosity decreases as a function of time followed by a rapid increase. The process is similar to that under nitrogen but insolubility must occur more rapidly. This is directly linked to the rate of elimination of HCl in oxygen because at equal degrees of unsaturation cross-linking is less important in an oxidising medium. They offered the following four mechanisms (1) copolymerisation between polyene groups (2) chain transfer between a polyene group and a segment of a normal chain (3) a Diels Alder reaction (4) cross dehydrochlorination between a point of high chlorine activity on one chain and hydrogen atom on another.

The kinetics of cross linking in solution was studied by Bengough and Sharpe[42] who arrived at the following expression for the cross bond formation

$$2.0 \times 10^{3}_{e}\ ^{-23000/RT}.c^{2}_{w}\ \text{crossbonds /1.sec.}$$

where c_w is the polymer concentration in monomoles/1 for polymers with number average degrees of polymerisation varying from 192-905. The overall energy of activation was found to be 23.0 $\pm$ 1 k. Cal/Mole, similar to that of dehydrochlorination. The addition of free radical initiators and inhibitors had little effect on the time of gelation whereas oxygen retarded or prevented gel formation.

The reaction is approximately second order with respect to polymer concentration as well as dehydrochlorination. The gel time varies inversely with the degree of polymerisation, $\overline{P}n$, and the rate constant for the cross linking decreases markedly with decrease in the value of $\overline{P}n$. However, the rate of cross bond formation does not depend appreciably upon $\overline{P}n$. Thus the probability of any individual structural unit under going cross linking is the same irrespective of whether it is part of a large or of a small polymer molecule. In contrast to dehydrochlorination these results indicate that allyl activation is of little or no importance in cross linking. A simple condensation reaction with the elimination of HCl seems to be the most reasonable mechanism. The cross linking reaction is to some extent energetically competitive with that of dehydrochlorination, however, due to differences in the concentration dependencies and in the frequency factors; the dehydrochlorination reaction is the faster process.

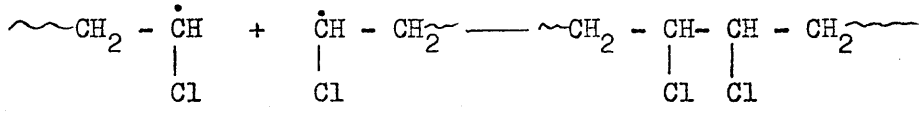
Polymer Intrinsic Factors influencing PVC Degradation:

1 - Chain Length and Molecular Weight. For low conversion polymers prepared by bulk polymerisation with azoisobutyronitrile, the rate was inversely proportional to the number average degree of

polymerisation[42]. Similar relationships have been noted for a series of commercially prepared polymers.[38,57] On the other hand, fractionated polymers showed no systematic dependence on intrinsic viscosity[44] and and inverse dependence in another study[49]. High conversion polymers were reported to have lower thermal stability[44] but for polymers prepared by solution polymerisation the reverse is true[68].

The contradictory results probably trace themselves back to differing degrees of unstable structures introduced under different conditions of polymerisation.

2 - Molecular Chain Order. Termination by combination leads to a vicinal dichloro structure caused by head to head linkage.



The presence of such links has been reported[69] and the instability of the structure has been demonstrated by degrading chlorinated trans 1 - 4 polybutadiene which is found to be slightly less stable than PVC.[70] According to Merk should a small proportion of alternating structures be present, the polymer chain would be much more susceptible to attack at the point where the two chlorine atoms are adjacent, a situation analogous to Flory's[71] findings with polyvinyl alcohols.

3 - Branching : Transfer to polymer occurs readily with PVC when the propagating radical abstracts a tertiary hydrogen atom either from its own chain or from another chain to leave a macroradical which is capable of continuing the polymerisation and forming a branch point[11,72].

Hence branch points in PVC would be characterised by a tertiary carbon-chlorine bond. If the polymerising radical is also capable of abstracting a chlorine or a secondary hydrogen atom, the result would be characterised by a tertiary carbon hydrogen bond at the branch point. Therefore, several different branch structures may be present in PVC.

Labile groups in PVC were detected by ester interchange[73]. This technique has shown that the reactivity of tertiary chlorines is greater than that of secondary species and that the former are concentrated in the high molecular weight material.[74] By analogy with their reactivity in heterocyclic reactions such as solvolysis[75], the tertiary carbon chlorine bonds are regarded as thermally labile under thermal degradation conditions. Gupta and St. Pierre[56] using model compounds such as poly-2-chloro propane further indicated their thermal stability.

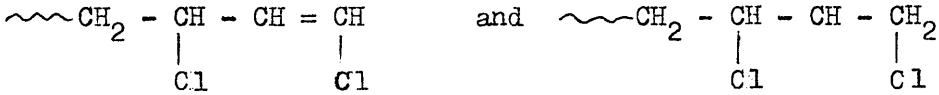
4 - Stereoregularity : Investigations have been made into the polymerisation of stereoregular enhanced PVC[28-30] and its effect on the consequent thermal dehydrochlorination, the most recent being the work of J. Millan et al[76] who found that the degradation rates of PVC were dependent on the syndiotacticity content. The kinetic results as well as the shape of UV-visible spectra of degraded polymers also suggest an influence of tactic sequences on the propagation step.

However, one should be aware that any increase in stereoregularity also brings other changes along such as in molecular weight, solubility and other parameters that could also affect degradation.

5 - Chain End Irregularities : If degradation is initiated at chain ends or by the vicinal effect of an end group, there would be a

relation between the rate of dehydrochlorination and the number of chain end groups and hence an inverse relation between the rate of dehydrochlorination and molecular weight. Such inverse relationships have been observed, but it can be shown that not all dehydrochlorination is initiated at chain ends[14]. Talamini[43] showed that after careful fractionation, there was an inverse dependence at low molecular weights but the rate of dehydrochlorination becomes constant for higher molecular weight fractions. This could be due to the presence of certain end groups to a greater extent in the low molecular weight fractions and these lead to the observed rate dependence on the reciprocal of the molecular weight, whereas the higher molecular weight fractions may contain fewer such end groups and hence will appear to be more stable. Chain end irregularities mainly fall into two categories, unsaturated end groups and initiator fragments.

Unsaturation. During polymerisation of vinyl chloride termination by disproportionation introduces two other types of end groups.



Unsaturated chain ends can also be formed by chain transfer to monomer reactions[11].

Terminal unsaturation causes allylic activation of the adjacent carbon-chlorine bond[36,25] forming sites for initiation of dehydrochlorination whether (according to Baum, eliminating allylic end groups reduced dehydrochlorination by 50%), by a uni-molecular or a free radical mechanism. The allylic activation causes the activation energy of the C-Cl bond scission to be lowered by about 19(k cal. $mole^{-1}$).[11] The reactivity of allylic chlorine structures has been

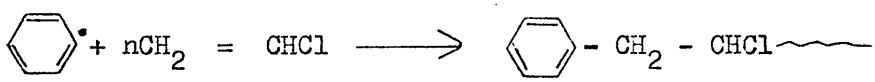
demonstrated in model compounds such as 3 - chloro-1-pentene, 3 chloro-2-pentene, 4-chloro-1-hexene and 4 chloro-2-hexene, which decompose more readily than the saturated analogues[77]. However, unsaturated compounds such as these model compounds are particularly prone to peroxidiation and a very small peroxide content would have a marked effect on their decomposition. Talamini[43] and Stromberg[36] suggest that free radical degradation is not very dependent on allylic activation. The high thermal stability of allyl chloride is in itself an argument against unimolecular elimination at chain ends in PVC[36] but the unsaturated groups may act as secondary sites in conjunction with occluded radicals[61] or with radicals from initiator fragments.

End Groups. If the polymerisation termination reaction is by combination there will be initiator residues at each end of the chain whereas if termination is by disproportionation then only one initiator fragment will occur per chain.

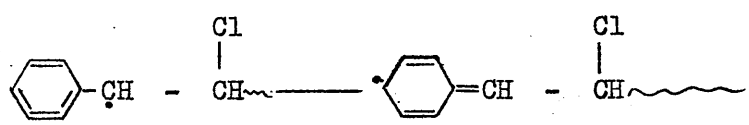
If no transfer reactions occur, a vast proportion of the chains will contain initiator fragments but due to the predominance of chain transfer reactions in the polymerisation of vinyl chloride, only 20 to 30% of the chain ends carry initiator residues[78]. Talamini[79] and Stromberg[36] found that the rate of dehydrochlorination varied with the initiator fragment present.
The latter show that initiator fragments may initiate dehydrochlorination by radical mechanisms by the dissociation of some weak bond in the initiator fragment to give an alkoxy radical and a macroradical from where the reaction schemes proposed by Arlman[80] and Winkler[81] may initiate.

Most recent work has shown that polymers prepared by free radical initiation in solution contain 0.5 - 1 initiator fragments per polymer molecule[82]. The fact that the end groups are a cause of dehydrochlorination initiation was shown in the case of lauroyl peroxide, isopropyl peroxydicarbonate, benzoyl peroxide and azoisobutyronitrile[68].

The azo compound can only initiate by addition to the monomer double bond[83] and hence produces the most stable polymer. Peroxide initiators may well undergo primary radical transfer to produce unsaturated end groups which would reduce polymer stability. In the case of benzoyl peroxide an additional possibility is initiation by phenyl radicals to give polymer with terminal phenyl groups



Instability at the chain end could then arise via the benzyl hydrogen atoms due to the possible resonance stabilisation of the resultant radical



External Factors Influencing PVC Degradation

1. Effect of Atmosphere

1.1 Effect of Hydrogen Chloride

Studies under HCl serve to clarify two basic phenomena observed by some workers, the first is that of induction period and second the possible autocatalytic effect of HCl.

The existence of a true induction period was first noticed by Havens[84] who explained it by suggesting that HCl does not appear until certain internal HCl concentration has been built up, leading to saturation. Druesdow and Gibbs[67] have shown that the reaction is independent of the ambient concentration of HCl, when carried under a nitrogen atmosphere while Scarbrough[85] arrived at an opposite conclusion. Imoto and Otsu[66] results supported Druesdow's et al findings. The influence of hydrogen chloride on the bulk dehydrochlorination of PVC is now generally accepted as being autocatolytic even in inert atmospheres[59,64,65,79,86-90], although recently[91] one report indicates that hydrogen chloride could inhibit the dehydrochlorination reaction in solution.

1.2 Effect of Oxygen

The presence of oxygen indisputably increases the rate of thermal dehydrochlorination in the bulk over that obtained under isothermal conditions in a nitrogen atmosphere.[25,42,57,67,80,92-96]

However different intermediary mechanisms are postulated, from carbonyl group formation[84], to the formation of water[66], peroxide formation and epoxides.

The effect of oxygen on colour is one of initial bleaching however, the greater hydrogen chloride evolution in air leads eventually to more rapid discolouration. Geddes[57] applied

intermittent atmospheres of oxygen and nitrogen during thermal degradation. He demonstrated that such active sites as may be generated[91,62] in the presence of oxygen have no permanent effect and are not comparable in their reactivity to those active sites already in PVC[97]. Evidence obtained from the oxidation of model polymers and fractionated PVC suggests that oxidation occurs preferentially at tertiary hydrogen.

2. Effect of Solvents

To avoid kinetic autocatalysis complication and in order to better investigate initial rates, PVC has been studied in solution.[44,92] The observed dependence of initial rate between different solvents was initially ascribed to a variation in the conformation of the polymer chains. Later Bengough and Varma[44] showed that activation energies for dehydrochlorination may be influenced by as much as 10 k cal/mole and it is now known[98,99], that interaction with solvent can affect degradation.

Marks et al[63] report a dependence of dehydrochlorination rates on the dielectric constant of the solvents in support of an ionic elimination mechanism[47].

3. Effect of Free Radical Initiators and Inhibitors

While the influence of oxygen is well known, the influence of peroxides[42,80,100] and other radical sources remains controversial. The increased rate obtained by Geddes[100] in the presence of AIBN has been criticised[47]. In agreement with Baum[92] pure AIBN was not found to have an effect.

There appears to be agreement that conventional radical inhibitors generally produce no effect on PVC dehydrochlorination, however, this might be anticipated since the mechanism of inhibitors

at 200°C is still an unknown. Nitric oxide has been suggested[60] as an ideal inhibitor, however this is uncertain especially as partially degraded PVC is discoloured by the same gas at room temperature. According to Neiman et al[88] the presence of nitric oxide was found to affect the rate of HCl evolution and was attributed to the formation of benzene free radicals.

A more recent and interesting development is the reporting[100] of the inhibition effects on dehydrochlorination by chloromercury acetaldehyde. It was concluded that in degrading PVC, chlorine atoms were present which react, with HgCl radicals to give mercuric chloride. This is the only instance that chlorine atoms have been identified in the dehydrochlorination reaction.

4. Effect of Degradation Energy Source

Photodegradation :

PVC is stable for years in the dark, but degrades in sunlight. This degradation is enhanced by subjecting it to UV radiation even at room temperature[102]. Scarbrough[85] believed that the UV light catalysed the reaction after a short induction period. Mack[103] suggested that after initial dehydrochlorination, oxidation of the chain took place. Winkler[81] has suggested a radical mechanism similar to the one discussed for thermal degradation.

Kenyon[142] found that the rate of dehydrochlorination was invariably proportional to the wavelength (3,400 to 2,350 Å). Here too degradation in an inert or vacuum atmosphere, causes an increase in molecular weight.

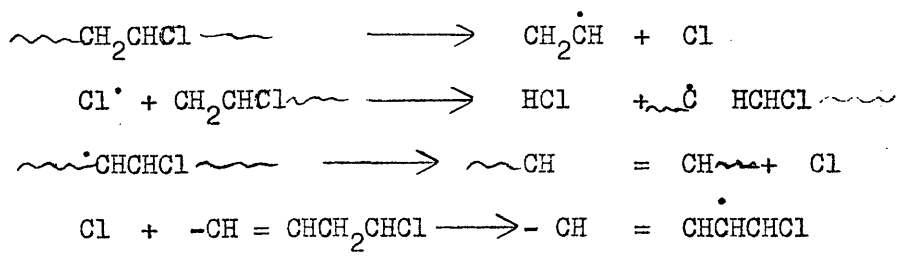
Havens[84] used the transmission of light as a measure of degradation, his work also suggested an isomerisation of the

polymers formed to the cis - form in sunlight and reversion to the more strongly coloured trans-form in darkness.

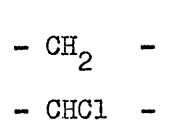
Recently more detailed work has been reported, of special interest is the study showing how oxygen accelerates photo decomposition and HCl inhibits it[104].

High energy degradation

When PVC is subjected to a beam of high energy electrons at low temperatures, a visible colour change takes place. Lawton et al[105] investigated the effect of high energy electrons on several polymers and observed that PVC degrades on irradiation. Chapiro[106] investigated this radiolysis of PVC in the solid state, and suggested the existence of 'frozen in' free radicals together with a polyene chain structure. Miller[107] explained the radiation and post irradiation effects observed for PVC on basis of a free radical chain dehydrochlorination, a mechanism similar to that of Winkler[81]. This process may occur as low as - 190°C but the radicals remain trapped. On warming to room temperature, free radical reactions occur according to :



Atchison[108,109] and Lay[110] through E.S.R. studies showed that on irradiation, several primary radicals are formed such as



and differentiated them as short, intermediate and long lived radicals. Some of the radicals could recombine to form cross links. He also observed that the concentration of colour producing material was inversely proportional to the concentration of long lived radicals a finding similar to that of Lawton and Balwit[111].

Proposed Mechanisms for the thermal Dehydrochlorination of PVC

Three distinct mechanisms have been proposed for thermal dehydrochlorination and all three have received recent support. Evidence has been presented for a 'Unimolecular' process with a cyclic transition state[47]. The autocatalytic effect of hydrogen chloride has been noted many times and has been cited as evidence that chloride ions are the active species in this autocatalytic 'ionic' degradation[90] though it has also been noted that hydrogen chloride can catalyse free radical decomposition[57]. Nevertheless ionic chain dehydrochlorination is readily promoted by the addition of a strong base[42,112]. 'Free Radical' chain processes have many supporters and it has been proposed that some of the different views might be reconciled if the reaction be considered a 'Non-Chain Free Radical' process as per Bengough and Sharpe[42].

1 - Unimolecular Elimination Mechanism :

If this was the main reaction one would expect the random elimination of HCl resulting in the random formation and placement of double bonds. This has been overcome by assuming allylic activation of the adjacent chlorine atom[25,67,113]. This accounts for the 'zipper' reaction which leads to long chains of conjugated double bonds. The loss of the first molecule of HCl would give a residual structure of

$$- CH_2CHClCH_2- \longrightarrow HCl + - CH = CH - CH_2 - CHCl-$$

$$- CH = CH - CH_2CHCl \longrightarrow HCl + \sim\!\!-CH = CH - CH = CH\sim\!\!\sim$$

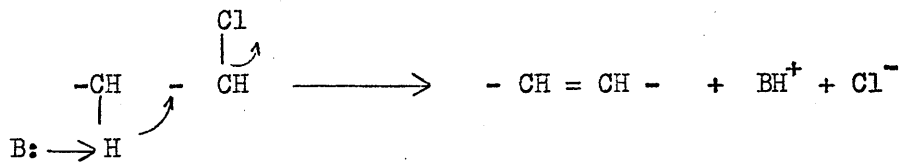
The Allylic activation would then cause the second molecule of HCl to be lost more readily, this process could then continue throughout the chain to form a long chain polyene of the nature $R\,(CH = CH - CH = CH)_n -$ which is responsible for the discolouration.

Termination of the reaction is believed to occur when it runs into a change in structure of the polymer chain either due to oxidation or branching. The evidence for the allylic chlorine being thermally labile is taken from heterolytic reactions such as solvolysis[114]. Allylic chlorines have also been shown to take part readily in ester exchange reactions[73]. Baum and Wartman, Grassie and Druesdow and Gibbs have supported this mechanism.

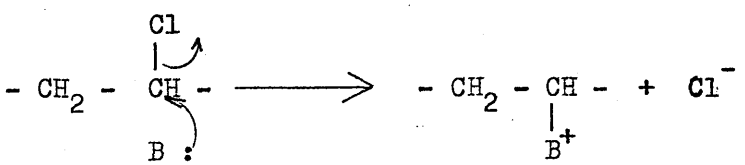
2 - Ionic Mechanism :

Under basic conditions alkyl chlorides undergo two reactions, elimination and substitution. Similar reactions are known to occur with PVC where elimination of HCl or substitution of the base for a chlorine atom are found.

Elimination



Substitution



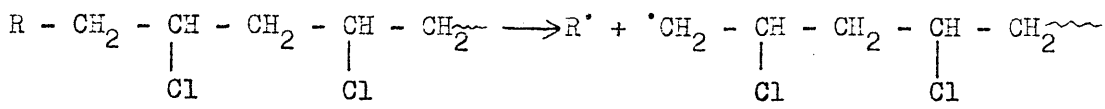
If the substitution reaction is suppressed, long chain polyenes result from this base catalysed dehydrochlorination.

This mechanism is confirmed by lithium chloride type reactions and sodium in liquid ammonia giving similarly coloured products as those experienced in PVC[115,116]. This reaction can occur in PVC under acidic conditions[117] as well as the original basic process[116].

3 - Free Radical Mechanism

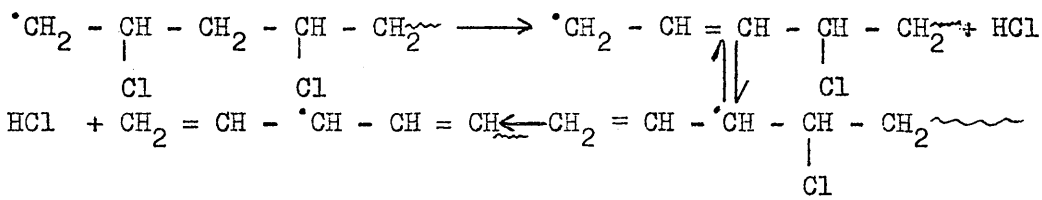
Arlmann[80] was the first to propose this mechanism based on the evidence that free radical initiators increase the rate of dehydrochlorination.

Initiation, is brought about by thermal cleavage of an end group



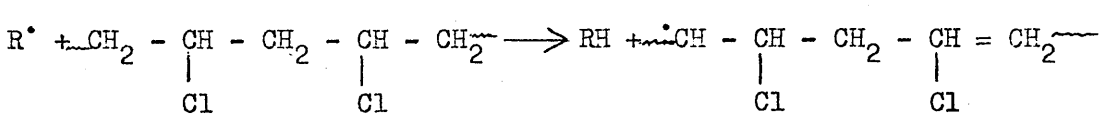
This is similar to the allylic activated molecular elimination in that the molecule of HCl is liberated from the monomer unit adjacent to the free radical. The unsaturated radical formed then rearranges to give a structure which can activate the elimination of another HCl molecule and this process is repeated until a long chain of polyenes is formed.

Propagation

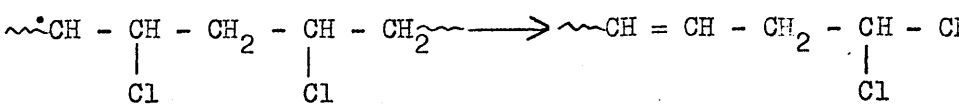


Recently radical mechanisms are getting their main support from ESR studies[118], however, this mechanism was also proposed by Winkler[81] in 1959 and Stromberg[36]. Winkler based his proposal on a similar mechanism for dichloroethane proposed by Barton and Howlett[119]. He suggested that initiating radicals could be derived from the catalyst residue or could arise as a result of oxidation. This initiating radical would then attack the methylene hydrogen atoms prefertially.

Initiation

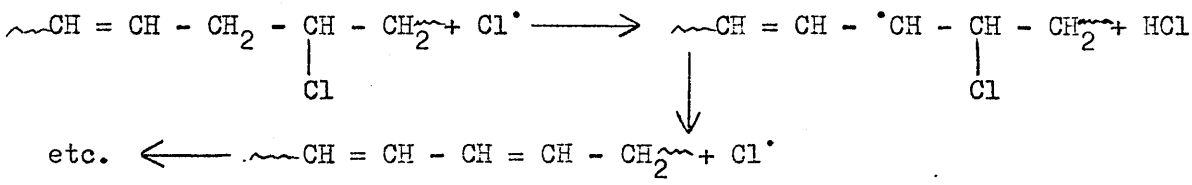


this macroradical rearranges to give a carbon-carbon double bond and a free chlorine atom.



The probability of the chlorine abstracting the neighbouring methylenic hydrogen rather than the secondary tertiary hydrogen is increased by its proximity to the double bond.

Propagation, is brought about by this second macroradical repeating the process in a chain type reaction which leads to a conjugated structure,



Stromberg and co workers[36] proposed a similar mechanism, except that they considered that the initiation step gave rise to a chlorine atom which goes through the sequence of methylenic hydrogen abstraction followed by rearrangement of the macroradical to give the double bond and another chlorine atom.

Termination, can occur by any of the following routes

(a) The chlorine abstracts a hydrogen atom from a carbon attached to a chlorine, a tertiary hydrogen, giving a $-\dot{C}(Cl)-$ radical which cannot continue the dehydrochlorination.

(b) The macroradical is oxidised.

(c) Via mutual termination of the chlorine atoms and the macroradicals.

(d) Abstraction of a hydrogen atom from another molecule by the chlorine atom.

Reactions a, b and d are also capable of restarting new chains and hence can be considered as chain transfer reactions.

CHAPTER 2

EXPERIMENTAL

MATERIALS

Vinyl Chloride, supplied by Distillers Co. Ltd. was found to be free from acetylenic impurities by gas chromatographic analysis and by chemical testing with aqueous silver nitrate solution. The monomer was collected from the cylinder in a cold trap on a vacuum line, degassed and stored as vapour in 5 - litre bulbs attached to the vacuum line. A final purity check was made by polymerising the monomer at 47°C in the presence of 1.15 mole % benzoyl peroxide for 1, 2 and 3 hours. The amount of polymer formed was in agreement with earlier work of Bengough and Norrish[11].

Benzoyl Peroxide (Bz_2O_2), from B.D.H. Ltd. was dissolved in chloroform and reprecipitated in absolute alcohol overnight.

1 : 1 Azobisisobutyronitrile (AIBN), from Eastman Kodak Ltd. was purified by recrystallisation from absolute alcohol.

C - 14 Labelled Benzoyl Peroxide, both carboxy - C-14 and ring C-14 labelled Bz_2O_2 were prepared from their respectively labelled benzoic acids obtained from the Radio-chemical Centre.

The labelled C-14 benzoic acid was mixed in each case with 30 gr. of dry pure crystalline benzoic acid and 22 cc. of redistilled thionyl chloride. The mixture was heated in a boiling, water-bath for one hour until no more hydrogen chloride evolved. The product (benzoyl chloride) was distilled at 194°C - 198°C. 30 cc of 4N/NaOH and 25 cc of redistilled benzoyl chloride were added alternately dropwise, into a beaker containing

50 cc of '40 - volume' H_2O_2, the temperature of the stirred reactants being kept below 8°C and slightly alkaline throughout. The solution was stirred for a further half hour after all the reagents have been added.

The flocculant precipitate was filtered off at the pump, washed with little cold water and then by absolute alcohol. The final product was purified by dissolving it in Analar chloroform at room temperature and precipitating it with absolute alcohol. The benzoyl peroxide product was then dried at room temperature under vacuum overnight. The final yield was 4 gr. of benzoyl peroxide. The purity of the compound was tested by IR, melting point (104°C.) determination and polymerisation rate tests.

C -14 - Labelled 1 - 1 - 'Azobisisobutyronitrile, this was prepared from 0.185 mole of hydrazine suphate, 0.37 mole of sodium cyanide and 0.33 mole of radioactive acetone of known activity from the Radio Chemical Centre, Amersham. On shaking an aqueous solution of the above for 2 days a crystalline material was obtained. The AIBN thus formed was filtered and recrystallised from absolute alcohol. The purity of the product was tested and found to have a melting point of 101.5°C.

Scintillation Fluid. This is made up of 3 gm. l^{-1} 2,5 - diphenyl-oxazole and 0.1 gm. l^{-1}, 1,4 - bis-(5-phenyloxazolyl benzene) in scintillation grade toluene supplied by Nuclear Enterprises Ltd.

Commercial Polymers, both suspension prepared PVC (JLB-49- Geon 111) and emulsion PVC (Pevikon) were supplied by Distillers Co. Ltd. These polymers were purified as described for the Laboratory prepared polymers.

Solvents and Reagents :

Tetrahydrofuran, from Eastman Kodak was dried over anhydrous calcium chloride for 24 hours and refluxed over ferrous - sulphate ($FeSO_4 \cdot 7H_2O$) for 6 hours under nitrogen before final distillation under nitrogen at 63°C - 64°C. The distillate could be used for a week if kept under nitrogen in dark bottles.

Cyclohexanone, (BDH grade) was purified by distilling under reduced pressure and filtered through a number 4 filter paper for viscometry.

Dimethylformamide DMF, (BDH grade) was freed of moisture by shaking with phosphorous pentoxide over five, one hour intervals followed by two distillations under reduced pressure and stored under nitrogen for no longer than one week. When used for viscometry it was filtered through a number 4 filter paper before use.

Ethyl Benzoate, B.D.H. grade with a boiling point of 212.6° C was used after distillation.

Ethyleneglycol, BDH grade with a boiling point of 198°C was used.

Sodium hydroxide, analytical reagent grade as supplied by BDH in concentrated volumetric solutions in polythene ampoules was used after proper dilution.

Chloroform, analytical reagent (A.R.) grade and
Methanol, from B.D.H.were used as supplied.

All other solvents for solution polymerisation were distilled before use under vacuum when appropriate.

APPARATUS

High Vacuum Line, this was built in Pyrex glass. It included two 5 - litre bulbs and a series of taps and traps arranged as shown in Fig. 2-1. The pumping system consisted of a three stage mercury diffusion pump backed by a rotary vacuum oil pump. A vacuum of about 5×10^{-4} mm. of mercury was maintained as measured by a calibrated Pirani gauge.

Dilatometers and Reaction Vessels, these varied in volume from 10 to 80 c.c. in capacity, and were constructed from Pyrex glass, (or from Carius tubing for thermal polymerisations above $60^{\circ}C$) consisting of a cylindrical bulb fitted to 1.5 or 2 m.m. bore Veridia capillary stem incorporating a constriction for flame sealing under vacuum and a B.10 ground glass cone for connecting to the vacuum line.

Thermostat, consisting of a thermostatically controlled circular Pyrex water bath contained in a copper jacket with fibre glass insulation in between. The required temperature was held to within $\pm 0.01^{\circ}C$ by a 60 Watt bulb heater operated by a relay circuit which was actuated by a mercury toluene regulator. For higher temperatures a Variac controlled 800 watt background heating coil was used. For long duration polymerisations a"Temp. unit - TU8"temperature controller was used.

For temperatures above $80^{\circ}C$ an oil bath consisting of a 5 litre beaker was used. This was thermistor controlled via a valve operated relay switch. This bath was wrapped by a wire mesh and polyurethane foam then fitted into a thick metal jacket.

For polymerisations at $0^{\circ}C$ and lower, a 'Minus Seventy Thermostat Bath' supplied by Townson and Mercer Ltd. was used.

U.V. Lamp, a 125 watt Osira mercury vapour lamp provided U.V.

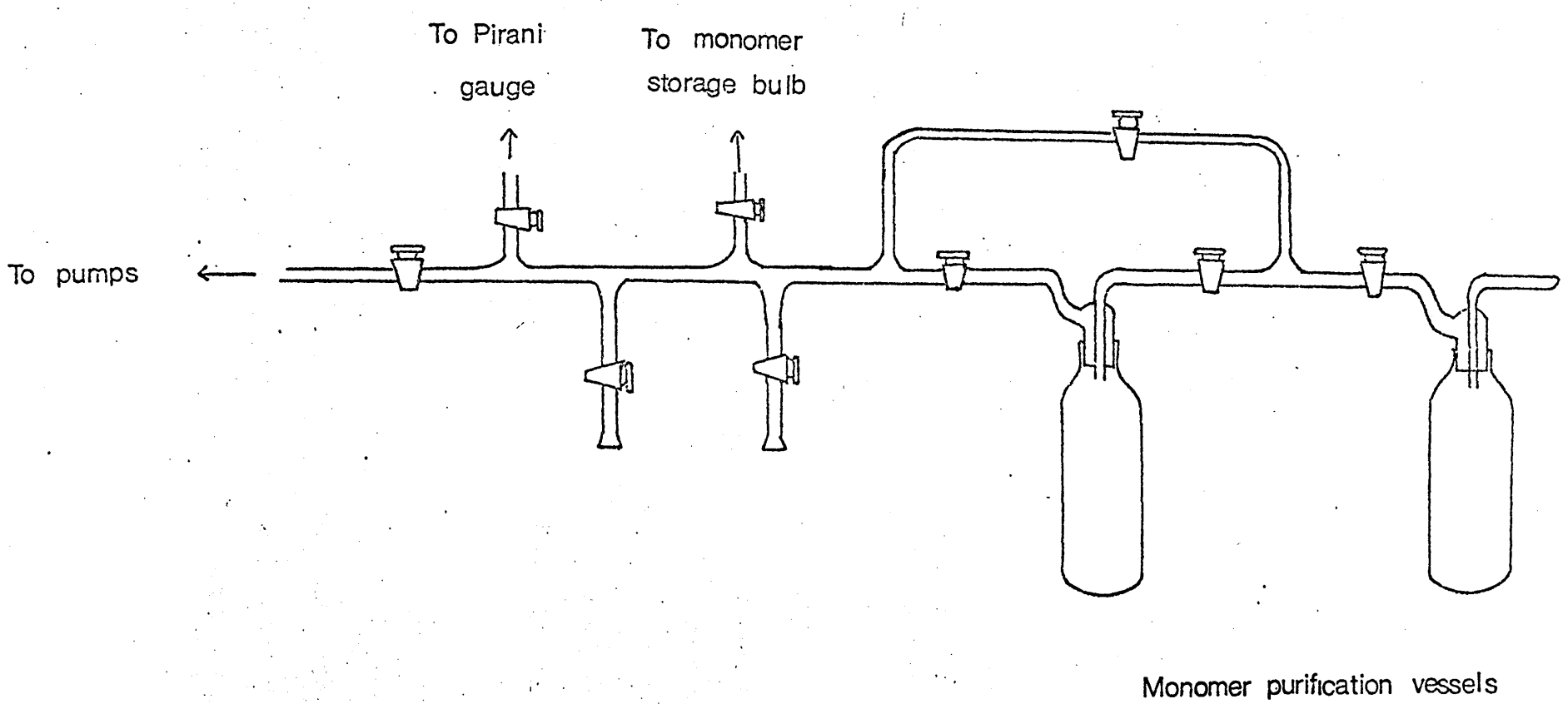


FIG. 2.1 VACUUM LINE

irradiation which was filtered through a Chance OX1 filter. The lamp was connected to a choke and capacitor to eliminate variations in the applied voltage. The light intensity was altered by inserting wire screens between the light source and the dilatometer.

Degradation Equipment, the pyrolysis unit used to carry out the thermal degradation in solution was a modified version of the one devised by Bengough and Sharpe[42]. The various parts of the unit are shown in fig. 2-2 and can be divided into three parts.

The vapour jacket or heater, consists of a cylindrical body with a side arm to receive a water condenser. It also contains a thermometer socket. The unit fits onto a round bottom flask. This flask contains the heating medium (solvent) and is heated by an electrothermal heating mantle. An asbestos coil or sheet is placed around the vapour jacket to prevent heat loss.

Secondly, the reactor was modified so as to confine the volume of displaced gases to a minimum, cut down on glass/reactants adsorption interface and lastly to allow us to scale down our reactants volume to a micro scale if needed.

The reactor is a Pyrex glass tube having a B-24 cone and socket as detailed in figure 2-2.

Thirdly the still head, was modified and it now comprises of two concentric glass tubes ending with a B 10 cone to fit into the B-10 socket, of the reactor. The inner tube was used for introducing the sweeping gas and the outer tube joined to the B-10 cone used for the transfer of the efluent gases to the recording system. At about $8\frac{1}{4}$" from the bottom of the B-10 cone a veridia capillary of 0.1 an I.D. was joined to the outer tube and used for the remaining of the afluent gas delivery system. A small water condenser was joined to the delivery tube above the B-24 socket.

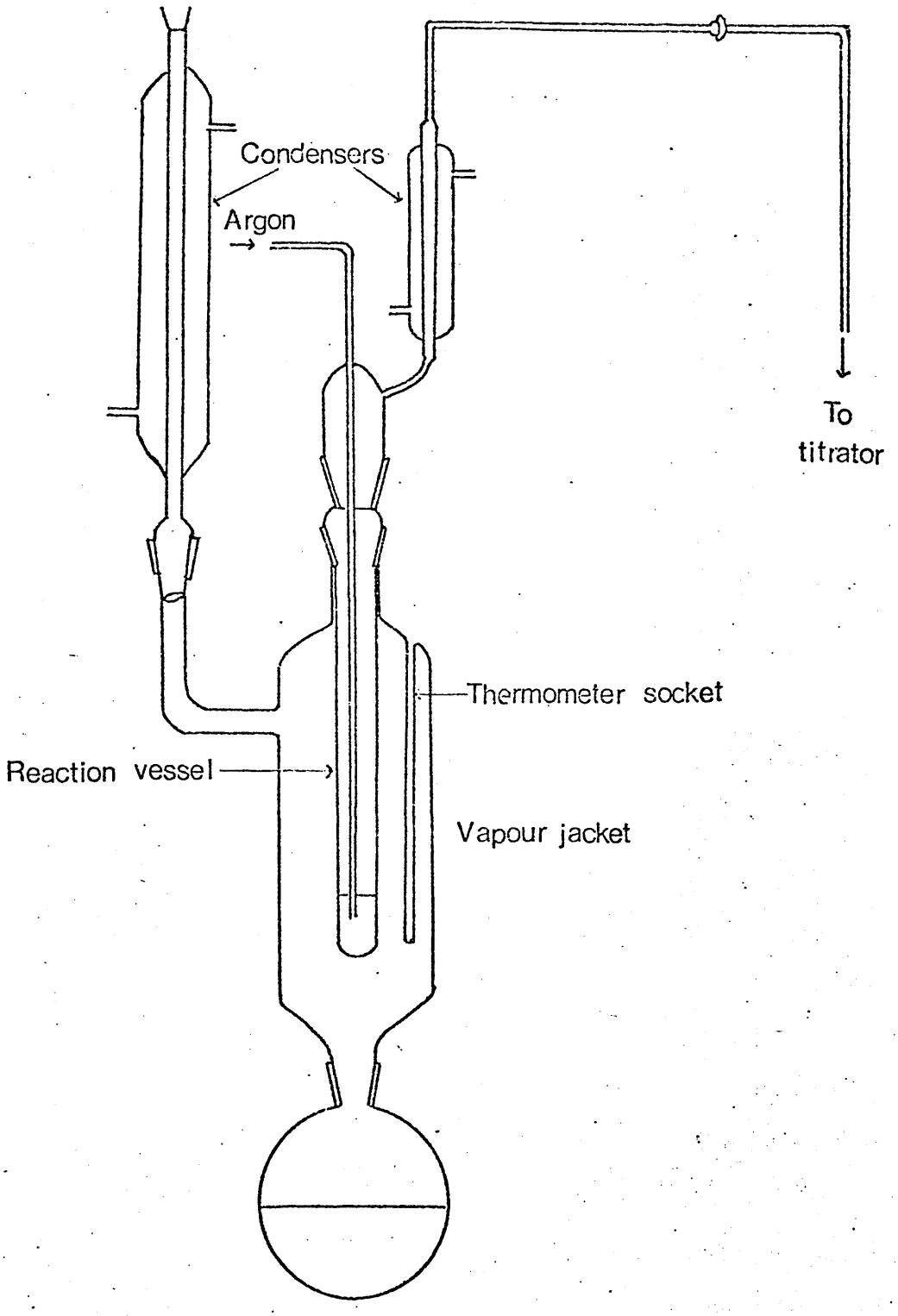


FIG. 2.2 DEGRADATION APPARATUS
(HEATING UNIT)

In modifying the system our aim was to build an inert all glass system, minimise displaced volumes and to optimise heat transfer.

The flow System. White spot high purity nitrogen gas was used for sweeping out the gases produced during the thermal degradation of the polymer. The flow was controlled by connecting a full nitrogen cylinder to an empty one which was used as a low pressure reservoir. Further flow of nitrogen is controlled by means of a needle valve and a micro guage.

The recording System. The progress of the reaction was followed volumetrically. Acid evolved during pyrolysis was swept into a glass cell containing distilled water and was titrated against N/400 sodium hydroxide automatically by the use of the 'Metrohm' Combititrator 3D. For extra visual inspection an indicator (bromothymol blue) was added to the distilled water.

To prevent the carbon-dioxide present in air to cause a pH change (6-7.6) in the distilled water, a distilled water trap was used.

The Combi Titrator automatically performs potentiometric titrations while recording the entire course of the titration, an end point at pH = 7 was chosen and the volume of reagent (N/400 NaOH) added against time (pH stat), was continuously plotted on the recorder.

The Combi-Titrator is composed of three elements, the direct reading line operated precision pH - meter E - 300, the impulsomat E - 373 (consisting of a pulse generator, a set point potentiometer with synchronous drive and an anticipatory circuit for the pre-set endpoint) and the Dosigraph E - 364 (recording piston burette).

The electrode used was a combined glass Universal, shock resistant, electrode (one unit electrode combining indicator and reference) with a range of application of 0 - 14 pH from 15°C to 100°C. and a standard

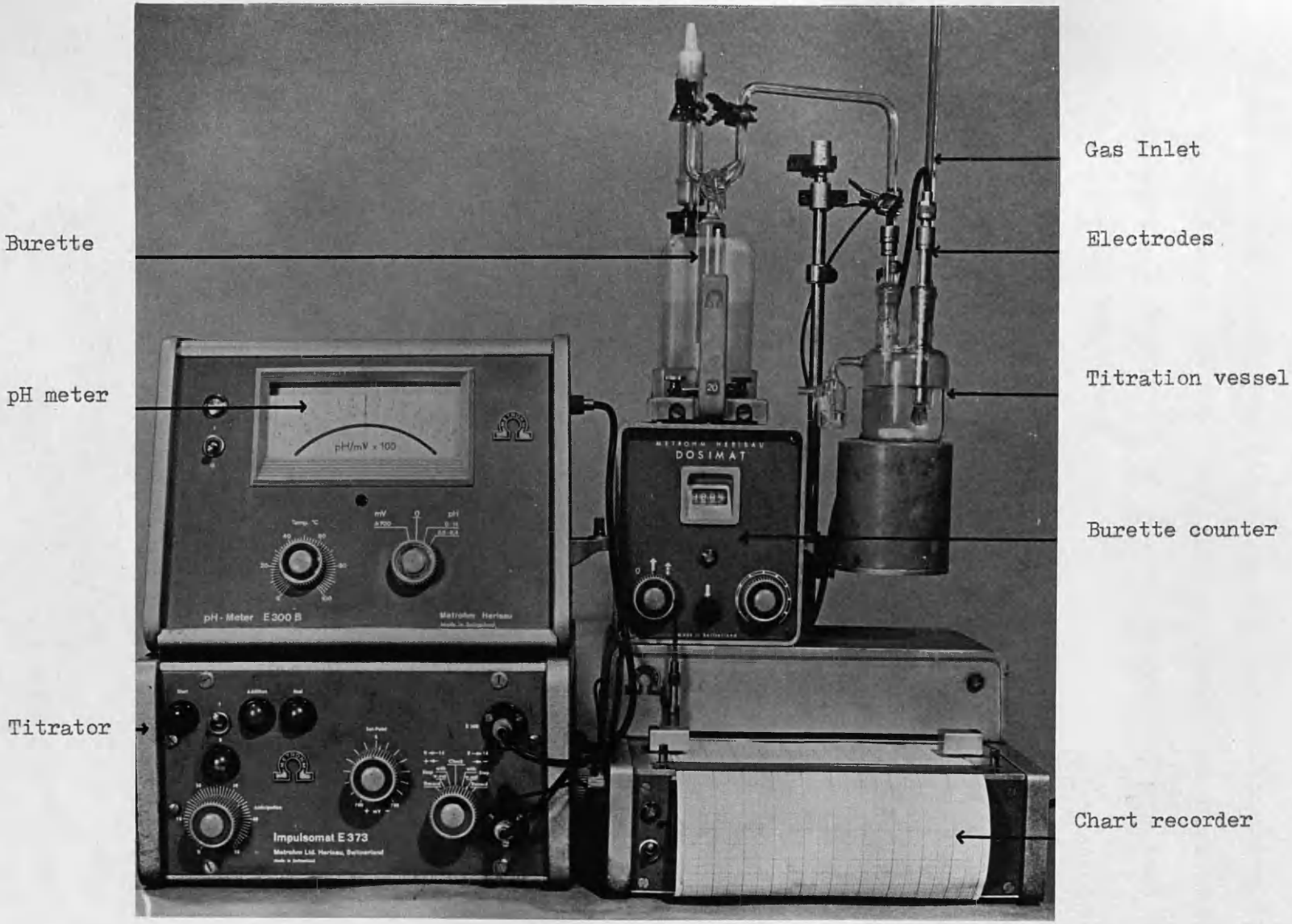


Fig. 2-3 TITRATION APPARATUS

membrane (10 m.m. diameter) of approximately 500 megohms at 20°C.

The combined electrode was fitted with a B-14 standard glass cone joint which fitted into one of the four sockets located on top of the glass cell containing the distilled water. The other three sockets held, a thermometer, the efluent gas delivery tube from the reactor and the burette tip.

The burette tip was modified by narrowing its orifice and bending the tip into a V-shape having the orifice $\frac{1}{8}$" above the water level facing upwards. This gave us much better control on drop sizes and also prevented the diffusion of NaOH from the burette tip.

The complete unit is shown in figure 2-3.

Liquid Scintillation Counting. The counting equipment used in the present work (supplied by Nuclear Enterprises Ltd.) consisted of a lead lined 'castle' incorporating the P.M. tube which housed the cells used to contain the sample and liquid scintillator.

The high voltage supply to the P.M. tube was provided by an E.H.T. unit and the output of the former was amplified by a linear pulse amplifier. A pulse height and gate width selector was incorporated for filtering purposes (see fig. 2-4).

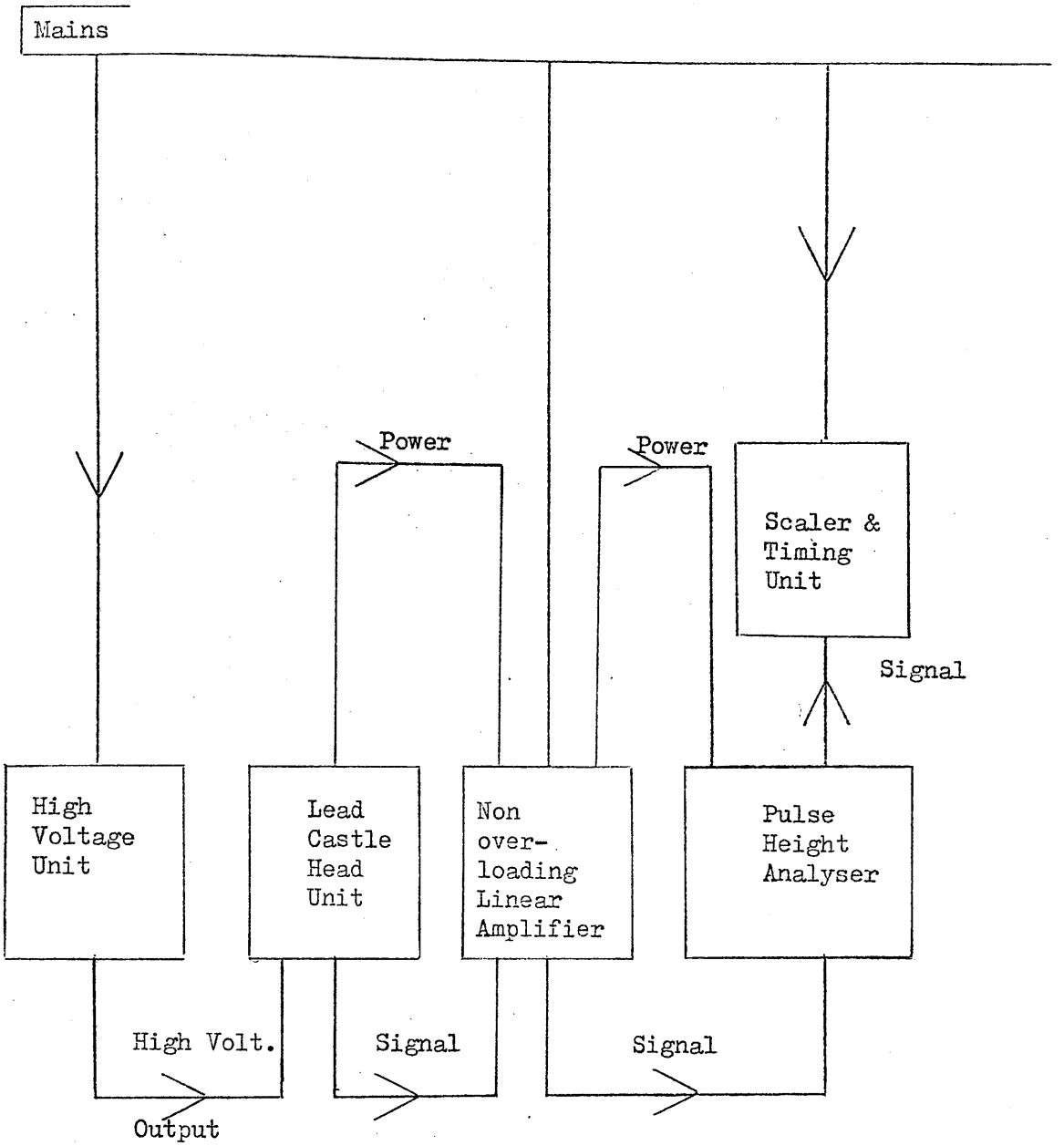


Fig. 2-4 - SCINTILLATION COUNTING EQUIPMENT CIRCUIT DIAGRAM

Osmometer. A high speed membrane Osmometer model 502 manufactured by Mechrolab Inc. was used. This consisted of a) an electronic section control unit b) the recorder Unit (Speedomex H) c) the elevator Assembly d) the thermostatically-heated sample block assembly.

An optical system in the solvent chamber detects flow through the membrane and automatically adjusts pressure by means of an electro-mechanical servo system to prevent any net flow. Since practically no flow of solvent is needed to establish osmotic pressure, the whole process takes only minutes and causes no dilution of the solution on the other side of the membrane.

PROCEDURES

Calibration of Vacuum Line and Dilatometers, given the volume of one of the bulbs on the line and by allowing the volume of air in the bulb to be shared with that part of the line and noting the pressure drop, it was possible to determine the volume of any part of the line. Boyle's Law was used for calculating the volumes.

Dilatometers(for following the rate up to 20% polymerisation) were calibrated at 25°C by filling via a capillary delivery to a mark on the stem with Analar acetone from a micro burette.

For higher conversions the rate was found gravimetrically.

The polymerisations were stopped at a precalculated time interval (so as to obtain Polymers with different specific conversions). A Percent Polymerisation-Time curve was drawn based upon the dilatometric results.

Bulk Polymerisations, for bulk polymerisations, the appropriate volume of initiator (either benzoyl peroxide or AIBN) solution was introduced into the dilatometer and the solvent pumped off gently especially at the final stages when the dry catalyst tends to spray out of dilatometer.

The bulb of the dilatometer was then immersed in liquid N_2, and on opening the vinyl chloride reservoir bulb the vapour rapidly distilled into the dilatometer. The volume of monomer condensed corresponded to the pressure drop on the calibrated manometer. Knowing the densities of the monomer liquid and its vapour, it was possible to calculate the exact weight of vinyl chloride added. Filled with the required quantities of the reactants, they were allowed to thaw and resolidify for a final check on the Pirani. The dilatometer was

sealed off and stored in a freezing mixture until required.

It was found to be more convenient in the case of big capacity dilatometers to distil pure liquid monomer to a micro graduated stemmed bulb first and then transfer it to the dilatometer.

Conversion and Rate Determination : Sealed dilatometers were submerged in a thermostat at designated temperatures. The rate of contraction of the polymerising system was followed in calibrated, narrow stemmed dilatometers using a cathetometer reading to 0.01 mm.

The volume-contraction conversion relationship was calculated at different temperatures by using the values of density of liquid vinyl chloride given by Dana et al[121] and a value of 1.403 for the density of polyvinyl chloride given by Distillers Co. Limited. The density of the polymer was assumed to be constant and the error involved in this assumption very small. The conversion factors found experimentally are given in Table 2-1 and are quite in agreement with those calculated from density measurements.

Table 2-1 - Density data for Vinyl chloride and Polyvinyl chloride for Calculation of Conversion Factors

Temp. C	Monomer Density grm/ml	Polymer Density grm/ml	% Conversion for 1% Contr. by Density Measurements	% Conversion for 1% Contraction Exp. determination
40	0.872	1.403	2.64	2.68
50	0.8517	"	2.55	2.60
60	0.831	"	2.46	2.46
70	0.809	"	2.36	2.32

Isolation of Products : When the required amount of conversion occurred the dilatometer bulbs were immersed in liquid nitrogen and the stem broken open. In case of solution polymerisations; the reaction mixture

was poured into a beaker and gently warmed to expel the unreacted vinyl chloride while for bulk polymerisations the unreacted vinyl chloride was distilled out on the vacuum line.

A dilute solution of the polymers was then made in freshly distilled THF. The optium concentration of the solution was found to be 12.5 gr/litre and was followed throughout our work for reproducibility purposes. It was found that above a 15 g/l concentration the PVC would aggregate into lumps. of solvent swollen polymer trapping impurities. Below a 12 g/l it would form a fine colloid very difficult to precipitate and to handle. The polymer was then precipitated into 10 fold excess of Methanol over THF. The Methanol was stirred with a partially immersed paddle so as to splash against the sides of the beaker and thus better dispersing the drops of solution falling into it. The process was repeated 3 times for most of the polymers. After the final precipitation the polymer was filtered off on a Porosity - 4 sintered glass funnel using a water pump while stirring the slurry at a constant rate in order to prevent the particles from coalescing. The polymer was then dried in vacuum for 24 hours at 40°C.

Solution Polymerisations, the same procedure as described for bulk polymerisation was followed with the following modification. The appropriate weight of initiator was first dissolved in the solvent to be used in the polymerisation process. The calculated quantity of solution was introduced into the dilatometer which was transferred to the vacuum line. The solution was frozen, the dilatometer evacuated and the solution allowed to thaw. This cycle of operations was repeated until the solution had been thoroughly degassed, as indicated by a constant low Pirani guage reading. All solution polymerisations were carried out at 60°C and the monomer concentration was kept

constant (50% by volume measured at 25°C). The concentration of the initiator, radioactive benzoyl peroxide, was 0.01 M% of vinyl chloride (or 0.0015 M/lt of total reactants) throughout. The solvents used were : isopropyl benzene, cyclohexane, chlorobenzene, dichlorobutane, bromobenzene, benzyl alcohol, ethyl benzoate, tritolylphthalate, dioctylphthalate, dibutylphthalate, tridecyl phosphite, diethyl phosphate, tetrahydrofuran, cyclohexanone, dimethyl formamide, pyridene, benzophenone, acetyl dimethylamide, nitrobenzene, Vinco, epoxyoctyl tallate, Mellite, dichloro-naphthalene and methyl iodide and where all freshly distilled and checked by refractive index tests.

Degradation, Description of a typical run. At the start of pyrolysis the heater was switched on. The apparatus was left for some time until thermal equilibrium was attained. A weighed quantity of polymer (usually 0.025 gr) was placed in the reactor tube (using a long delivery tube in order to avoid polymer adhering to the upper glass walls of the reactor due to static) and dissolved in 1 c.c. of solvent by warming giving us a concentration of 25 gr/lt. The reactor tube was then connected to the nitrogen gas flow system by inserting the B - 10 cone of the nitrogen flow tube. The reactor was then flushed in cold by nitrogen and connected to the combi titrator glass cell and left for five minutes to reach pH equilibrium. The reactor is then placed in the vapour jacket for 15 seconds, removed and shaken in ice for 60 seconds. The reactor was then replaced in the vapour jacket (maintained at 198°C by boiling ethylene glycol) and the run started. After one hour the run was stopped and the reactor immersed in ice/water. The flow time of nitrogen was usually checked at least three times during the run. In some cases the degraded polymer in solution was preserved

for further analysis. The optimum Combi Titrator settings were found to be,

Set pH at 7.0	Calibrated pH of 7.035
Fine range (5.6 $\longrightarrow$ 8.4)	Temperature set at 26°C
Selector 'Without Stop'	Anticipation - maximum
Burette speed- minimum	Burette additions - continuous
Stiring - using 1.5" magnetic flee at $\frac{3}{4}$ speed	Recorder paper speed - 2 mm/min.

and consequently were used throughout our work.

It was also found that the nitrogen needed to be passed through concentrated Analar sulphuric acid trap followed by distilled H_2O and silicagel to obtain a blank pH of 7.0. The nitrogen was passed at a rate of 1.8 bubbles per second.

Liquid Scintillation Counting, In this technique, use is made of the photons created when a suitable luminescent material is excited by nuclear radiation. These photons are collected at the cathode of a photo-multiplier tube which converts them into electrons. Multiplication of these electrons in the photomultiplier gives rise to electrical pulses which can be recorded on the normal scaler and timing unit. Each isotope produces a typical pulse dependant on its energy output and a discrimination is introduced into the circuit to differentiate between spurious pulses and those due to the presence of the isotope.

Counting was carried out on samples dissolved in 5 ml. DMF which were added to 5 ml scintillator solution in the silica cells. Background counts were taken using 5 ml pure DMF and 5 ml. scintillator solution only.

Satisfactory counting conditions were found by varying the E.H.T. voltage for constant amplifier gain, pulse height and gate width

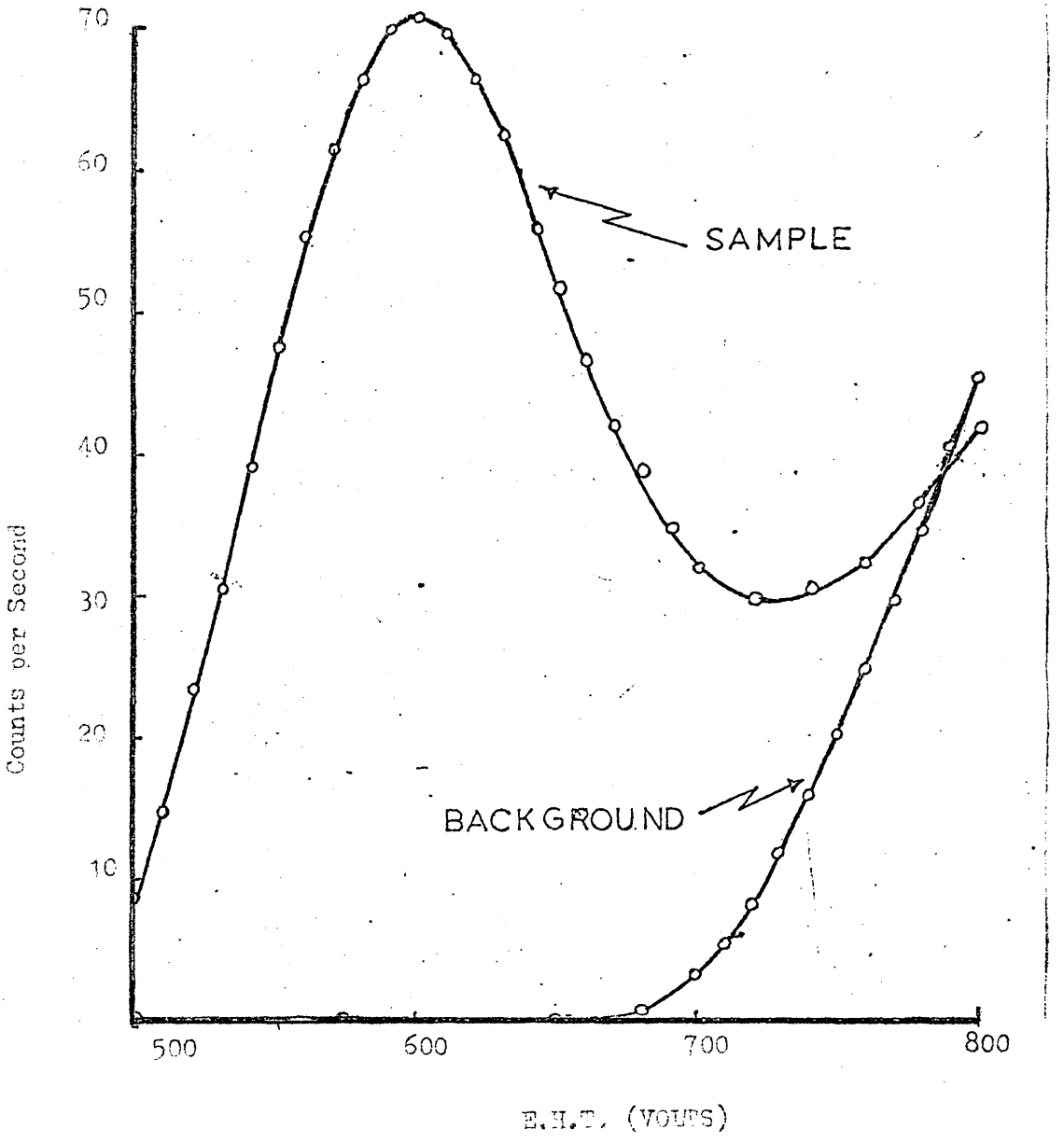


Fig. 2-5 COUNT Vs. E.H.T.

settings and taking measurements of the registered activity of a radio-active sample and of background. The other variables were held at the following constant values

Amplification	20 x 1
Pulse Height	10 volts
Gate width	30 volts

on the basis of these results counting was carried out at an E.H.T. setting of 600 volts. The calibration curve shown in Fig. 2-5 was arrived at by counting on 5 ml. samples of DMF solutions of increasing concentrations of the radio-active solution.

Viscometry, the intrinsic viscosity of the polymers was determined at 25°C using a suspended level modified Ubbelhode viscometer. PVC solutions of 0.4 grams per 100 c.c. concentration was obtained by dissolving a weighed amount of polymer in solvent, shaking it for 24 hours followed by centerfugation at 700 rps for 15 minutes to remove microgels and dust particles. Dilution of the polymer solutions was carried out in situ and the flow times were measured for both the pure solvent and a series of different polymer concentrations. The intrinsic viscosities of the solutions were calculated from the general equation

$$[\eta] = \lim_{c \longrightarrow 0} \frac{\eta_{sp}}{c}$$

Osmometry. The principal method for determining the number average molecular weight $\overline{M}n$ for high molecular weight polymers is by osmotic pressure measurements. A semi-permeable membrane divides a container into two compartments, one containing solvent and the other the polymer solution. At constant temperature and pressure, the chemical

potential of the pure solvent exceeds that of the solvent in solution. This difference in chemical potential causes solvent to flow through the membrane into the solution compartment. By increasing the pressure on the solution, the difference in chemical potential can be eliminated and net transfer of solvent through the membrane reduced to zero. The pressure applied is therefore the osmotic pressure of the solution. Four types of membranes were tested :

1 - Ultra cellafilter (regenerated cellulose) Feinst grade (Membranfiltergesellschäft Gottinger, Germany)

2 - Gel cellophane 300 grade (American Viscose Corporation)

3 - Gel Cellophane 300, and 600 grade (British Cellophane Ltd.)

4 - Schleicher and Schnell SGC grade (UFF/AG)

After testing the above membranes for solvent permeability, assymetry and retentivity, the Schleicher and Schnell were found to be the most suitable for our work.

The membranes were conditioned according to Table 2-2.

Table 2-2 - Conditioning Schedule for Osmometer Membranes.

Time (hrs)	% Water	% Acetone	% Solvent
	100*		
1	75	25	
1	50	50	
1	25	75	
1		100	
1		75	25
1		50	50
1		25	75
16			100 **

* Used for initial storage of membranes 0.01 g Hyamine 1622 (Lenning

Chemicals Ltd.) added per 100 c.c. of solution to act as membrane preservative.

** Membranes stored in fresh solvent after 16 hours

Molecular weight standards were used for testing retentivity of the membrances. These were polystyrenes.

Standard Reference Material No. 705 which is a narrow molecular weight distributive polymer (Mz : Mw : Mn = 1.12 : 1.07 : 1) where Mw is about 170,000. The other is No. 706 which is a broad molecular weight distributive polymer (Mz : Mw : Mn = 2.9 : 2.1 : 1) where Mw is about 260,000.

Supplied by the U.S. Department of Commerce.

Analytical Fractionation and GPC . Selected polyvinyl chloride samples were analysed on a Waters Gel Permeation chromatograph at 25°C in tetrahydrofuran as solvent.

These analysis were performed by Dr. W.W. Kerr of Distillers Company Limited, Epsom, Surrey.

A 1% solution of Polymer in THF was injected into a stream of THF (being pumped at a rate of 1 ml/min) through a series of five columns of cross-linked polystyrene gel arranged in decreasing order of porosity (10^6, 10^5, 10^4, 10^4, 10^3A°), and analysed by detecting the concentration of polymer in the effluent stream by means of a differential refractometer. In such a system the higher the molecular weight of the solute the less able it is to penetrate the polystyrene gels and the sooner it is eleuted from the column system. The chromatogram abscissa quoted as count numbers, where each count corresponds to 1 ml. eluted, is thus a measure of molecular weight, the logarithm of molecular weight being an approximately linear function of count number. The chromatogram ordinate is proportional to the difference

in refractive index between the eluent stream and the reference solvent stream. Since this refractive index difference is proportional to the concentration of polymer in solution and is independent of molecular weight, the chromatogram effectively reflects the polymer molecular weight distribution which may be derived from it by calibration with standards of known molecular weight.

The column system used in the analysis of the polymers was calibrated using anionically polymerised polystyrene standards, and a graph drawn of effective chain length as ordinate against count number as abscissa. The effective chain length is calculated using the accepted values of C-C and C-H bond lengths and inter bond angles, assuming the polymer chain to have an extended planar zig-zag configuration. Although this is quite empirical in concept, it does, however, enable a single calibration curve to be drawn up from which the molecular weights of various polymers can be derived on the basis of defining a molecular weight per angstrom unit; 41.35 for polystyrene and 24.85 for polyvinyl chloride. Since molecules are in fact eluted on the basis of their hydrodynamic volumes in solution this concept can be regarded as nothing more than a rough approximation. The molecular weights quoted for the samples should not therefore be regarded as absolute values.

CHAPTER 3

PREPARATION AND CHARACTERISATION OF PVC

Free radical polymerisation involves a series of reactions whereby free radicals are produced (initiation) a macromolecule is built up (propagation) and then the free radicals are deactivated (termination). These reactions can be subjected to a detailed kinetic analysis as touched upon in the introduction.

The unique properties associated with a polymeric material depend on its molecular weight, the strength of its intermolecular forces, the regularity of the chain structure and the flexibility of the main chain. In polymers, the inter and intra molecular reactions between the individual repeating units are able to exert a cumulative effect by virtue of their combination into a covalently bonded chain structure. Consequently, the molecular weight of a polymer is of prime importance in its synthesis and application.

Polymers are polydisperse or heterogeneous in molecular weight because of the statistical nature of their polymerisation, and therefore molecular weights should be considered as being averages otherwise the exact distribution of the molecular weights within the polymer must be determined. Also, different methods of determining the molecular weight of a polymer samples yield different average molecular weights, the most important of which are the following.

1. The number - Average Molecular Weight, $\overline{M}n$ mainly determined by osmotic pressure measurements, is defined as the total weight, w, of all the

molecules in a polymer sample divided by the number of molecules present. Thus, the $\overline{M}n$ is defined by

$$\overline{M}n = w/\Sigma N_x = \Sigma N_x M_x / N_x$$

where the summations are over all the different sizes of polymer molecules from X = 1 to X = ∞ and N_x is the number of molecules whose weight is M_x.

2. The Weight - Average Molecular Weight, $\overline{M}w$, obtained from light scattering measurements, is defined as

$$\overline{M}w = \Sigma N_x M_x^2 / \Sigma N_x M_x$$

where W_x is the weight fraction of molecules whose weight is M_x

3. The Viscosity-Average Molecular Weight, $\overline{M}v$ is obtained from viscosity measurements and is defined by

$$\overline{M}v = \left[\Sigma N_x M_x^{a+1} / \Sigma N_x M_x\right]^{1/a}$$

where a is a constant. The viscosity and weight - average molecular weights are equal when a is unity. However, $\overline{M}v$ is almost always less than $\overline{M}w$ since a is usually in the range of 0.5 to 0.9.

More than one average molecular weight is required to reasonably characterise a polymer sample. The determination of the changes in number - average molecular weight by viscosity measurements alone may be impossible due to the presence of chain transfer to polymer reactions which will affect the intrinsic viscosity of a polymer but should have no effect on its number - average molecular weight.

Consequently, for polymers produced under conditions where chain transfer to polymer may occur, the constants in the Mark Houwink equation are invalid and consequently changes in the intrinsic viscosity of the polymer have been reported rather than the changes in the molecular weight. Characterisation of a polymer by number - average molecular weight alone, can also be extremely misleading since most

polymer properties are determined by the size of the molecules which make up the bulk of the sample by weight. However, the changes which occur in the intrinsic viscosities and the number - average molecular weight of polymers produced under different conditions can lead to a better understanding of the polymerisation process. Such determinations can give indications as to the effect of chain transfer reactions and the reasons for the non ideality of the kinetics of the polymerisation.

The main interest in this project was not the kinetics of polymerisation of vinyl chloride but the thermal degradation and hence the stability of the polymers as affected by varying the controlled conditions of polymerisation. Consequently, this study has not been a systematic investigation into the kinetics of the free radical polymerisation of the monomer.

The main effort was concentrated on the free radical bulk polymerisation of vinyl chloride using, mainly C^{14} labelled Bz_2O_2 and to a much less extent AIBN at three different initiator concentrations of 1.0, 0.1 and 0.01 mole %. Polymerisation temperatures were varied and in some cases covered the range of + 140°C to - 75°C. Polymers with varying degree of conversion were also prepared. An attempt was made to compare polymers prepared through different techniques other than thermally induced bulk polymerisation such as, photo-initiated bulk polymerisation, thermally induced solution polymerisation and both commercially prepared emulsion and suspension polymers.

Results

Bulk polymerisation of vinyl chloride

PVC was prepared by bulk polymerisation of vinyl chloride using Bz_2O_2 and, in some cases, AIBN as initiators at different

temperatures. The rate of polymerisation was followed dilatometrically to predetermine different percent conversions and then polymerisations were repeated for each different percent conversion and rates calculated gravimetrically. In all cases, it was the initial average rate of polymerisation, to a conversion to polymer of approximately 5% which was measured.

Rate dependence on Bz_2O_2 Initiator concentration.

Figure 3-1 illustrates the dependence of the rate of polymerisation of vinyl chloride on the concentration of Bz_2O_2 (1.0, 0.1 and 0.01 m %). It can be seen that in each case an auto-catalytic effect manifests itself appearing to be more prevalent in the lowest concentration. Also the rate falls off after this effect, at about 75%, 65% and 55% conversion for the 1.0 Mole %, 0.1 Mole % and 0.01 M% initiator concentration respectively. The plot of average rate of polymerisation up to five % polymerisation at 60°C against the square root of the concentration of Bz_2O_2 is given in figure 3-2 and indicates a linear relationship.

Rate dependence on temperature of polymerisation using Bz_2O_2 as initiator.

The rate of polymerisation increases markedly with increase in temperature as evident in figure 3-3 which shows the course of the polymerisation of vinyl chloride catalysed by 0.01 M% C^{14} labelled benzoyl peroxide at temperatures of 25, 40, 60,°C.

When the logarithm of the average rate of polymerisation over the first 5% polymerisation is plotted against the reciprocal of the absolute temperature an overall activation energy of 17.4 k cal/mole (fig. 3-4) is obtained. This is considerably lower than the value of

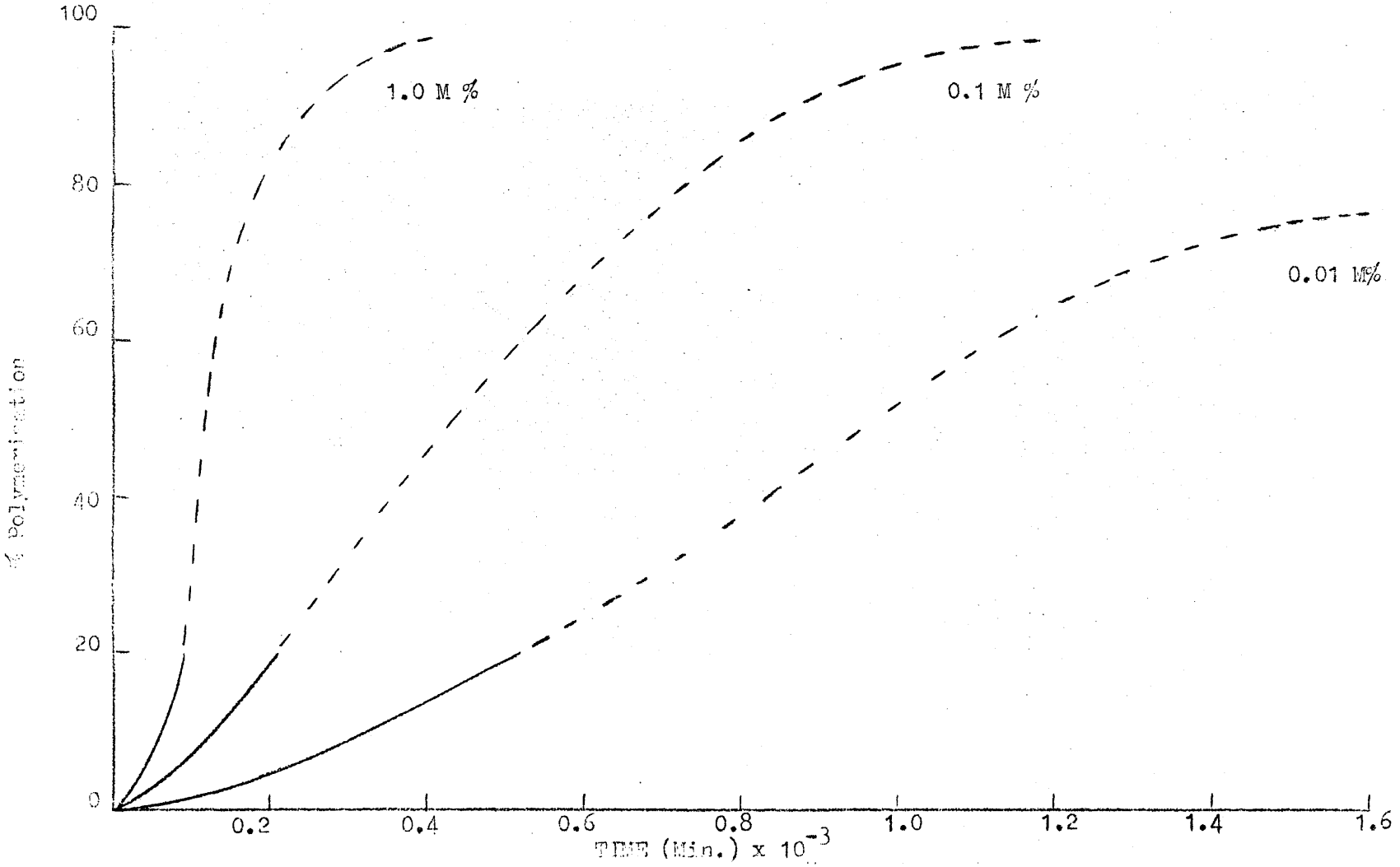


FIG. 3-1. BULK POLYMERIZATION OF VINYL CHLORIDE at 60°C with 0.01, 0.1 and 1.0 M% Bz_2O_2
(Solid line Conversion through Dilatometry
Dashed line Conversion through Gravimetry)

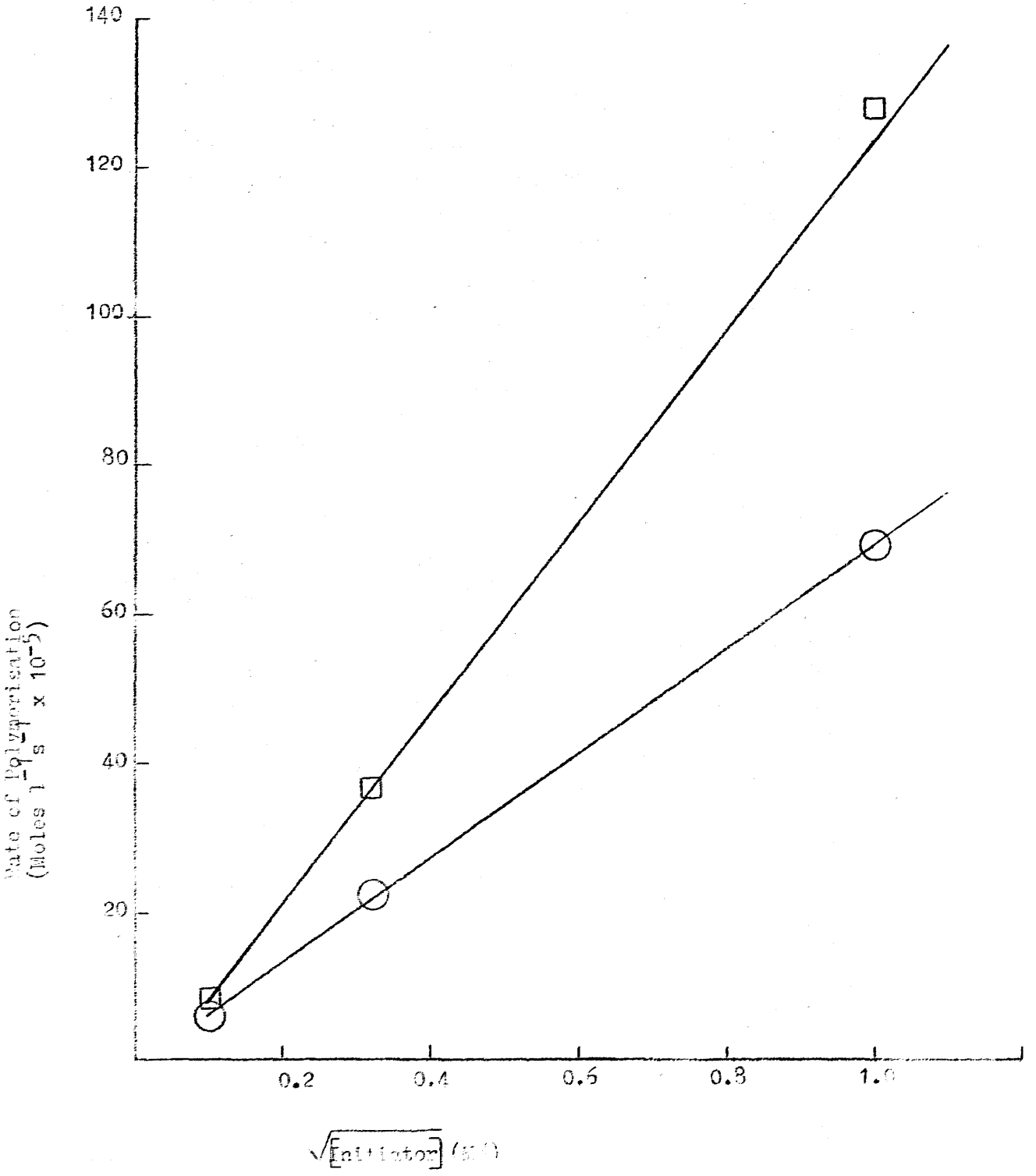


Fig. 3-2 RATE DEPENDENCY ON INITIATOR CONCENTRATION
(—□—□— $P_2O_8^{2-}$, —○— AIBN)

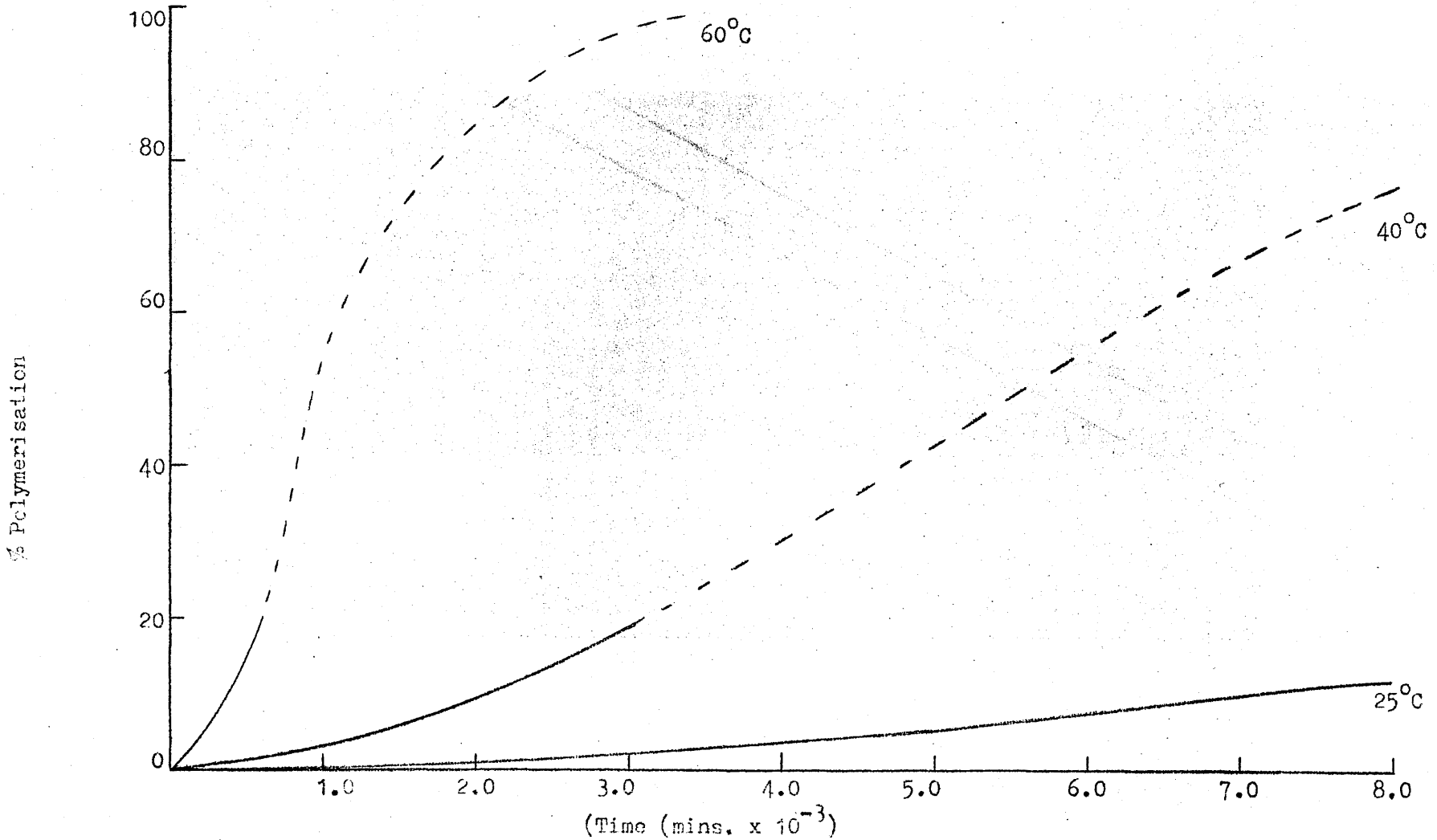


FIG. 3-3 BULK POLYMERISATION OF VINYL CHLORIDE at 25°C, 40°C and 60°C using 0.01 M% Bz_2O_2
(Solid lines conversion through dilatometry
Dashed lines conversion through gravimetry)

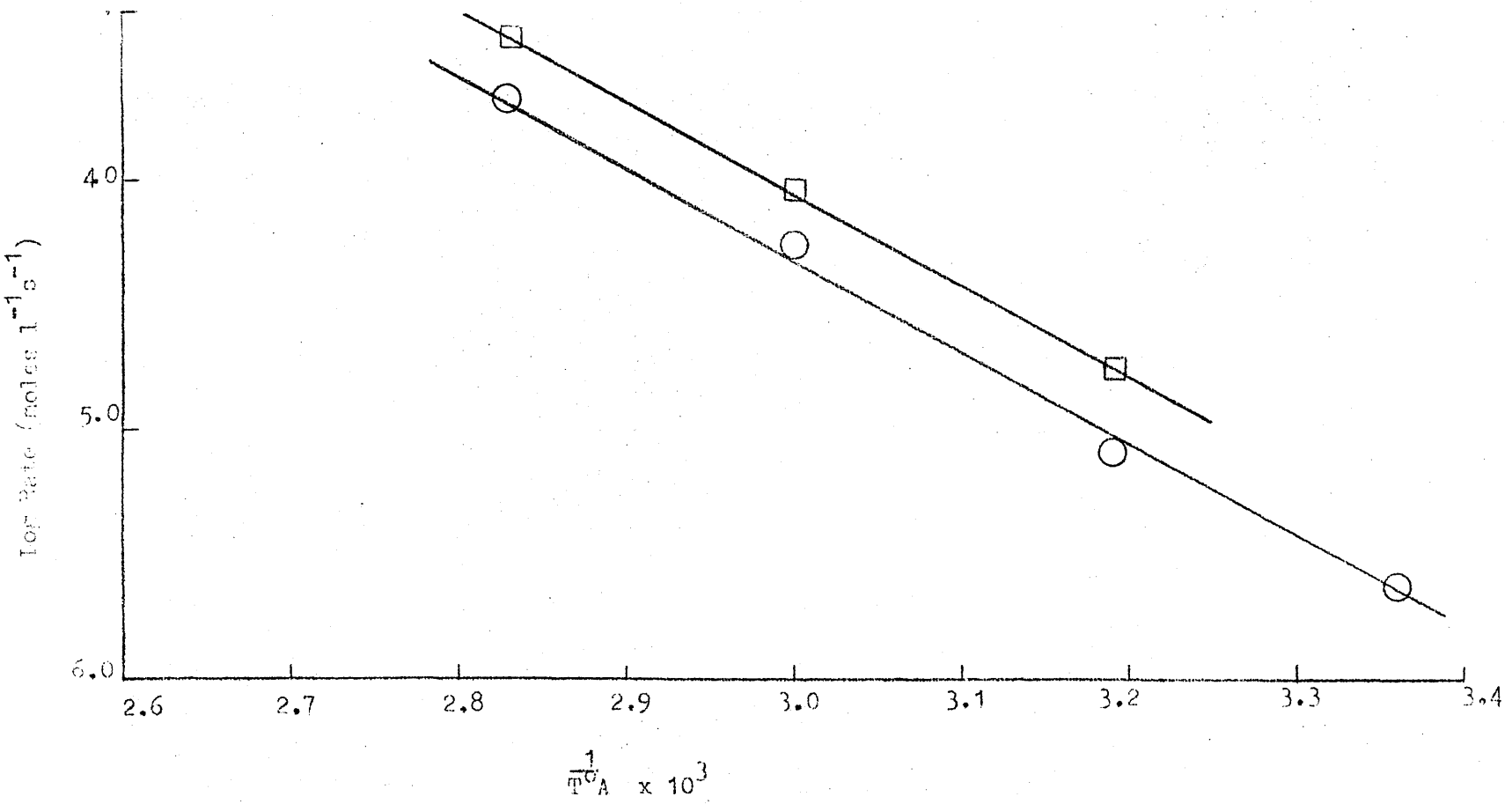


Fig. 3-4 OVERALL ACTIVATION ENERGY FOR THE BULK POLYMERISATION OF VINYL CHLORIDE -o-o- Bz_2O_2 and -□-□- AIBN

21.8 k cal obtained by Bengough and Norrish[11].

This could be due to a number of reasons :

1 - In this work the benzoyl peroxide was prepared in the laboratory using C - 14 benzoic acid and may possibly have contained some impurities which may have affected its decomposition. The decomposition of benzoyl peroxide is known to be affected markedly by some solvent impurities.

2 - Instantaneous rates were used by Bengough and Norrish whereas average rates have been used in the above results. These might differ slightly because of the autocatalytic effect.

3 - The use of large dilatometers in this study might have induced self heating effects, but this is unlikely as this would probably tend to form a high activation energy.

Rate dependence on AIBN Initiator Concentration

Figure 3 - 5 illustrates the dependence of the rate of polymerisation of vinyl chloride on the concentration of AIBN for 1.0, 0.1 and 0.01 M%. Although the rates are faster for AIBN initiated polymerisations, the autocatalytic affect is still evident and is similar to that experienced with Bz_2O_2. The plots have a similar shape, comprising of a relatively slow rate induction period followed by propagation and the autocatalytic effect and a final flatening of the shape as termination occurs. Although the rates were faster, the autocatalytic segment of the curve ends earlier in the case of AIBN than in Bz_2O_2.

The reaction order with respect to initiator was 0.5 as determined by the linearity fit when polymerisation rates at 60°C are plotted against the square root of initiator concentration fig. 3-2.

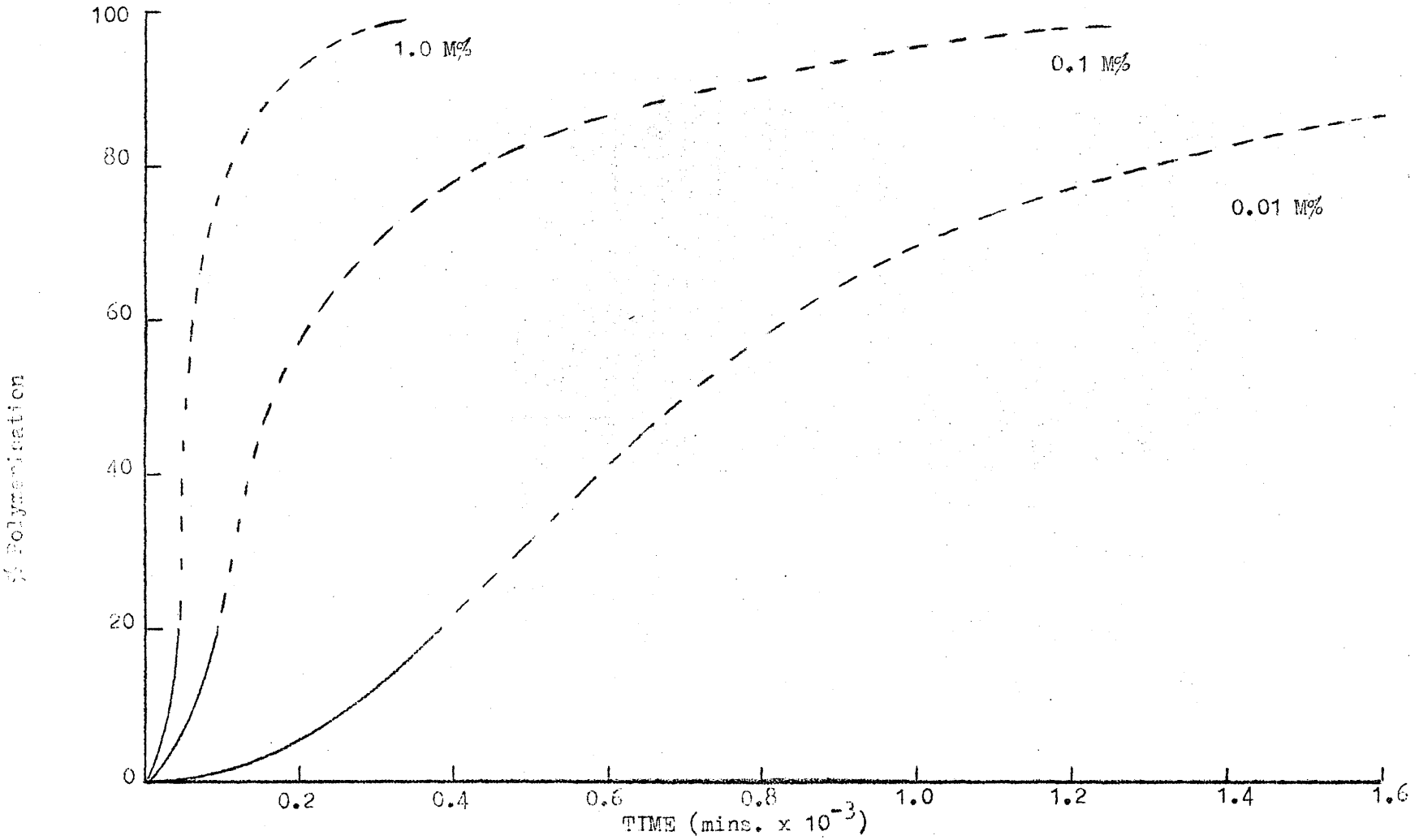


Fig. 3-5 BULK POLYMERIZATION OF VINYL CHLORIDE at 60°C with 0.01, 0.1 and 1.0 M% AIBN
Solid lines, Dilatometric conversion measurements
Dashed lines, Gravimetric conversion measurements

Rate dependence on temperature of polymerisation using AIBN initiator

The rate of polymerisation increases with increase in temperature as evident in figure 3-6 which shows the course of polymerisation of vinyl chloride catalysed by 0.01 M% C^{14} labelled AIBN at temperatures of 40, 60 and 80°C.

The overall activation energy of polymerisation was calculated from the log (rate) versus reciprocal absolute reaction temperatures plot shown in figure 3-4 and was found to be 16.2 k cal/mole.

Table 3-1 compares the rate of polymerisation up to 5% conversion in terms of moles of monomer removed per litre per second of both 0.01 M % AIBN and Bz_2O_2 initiated polymerisations.

At these initiator concentrations the AIBN rate is greater by a factor of about 2.0 over the temperature range of 40 to 80°C.

Table 3-1. Effect of type of initiator on the average rate of polymerisation.

Temperature of Polymerisation °C	Time to 5% Conversion Mins.		Average Rate l^{-1} s^{-1} x 10^5 moles	
	AIBN	Bz_2O_2	AIBN	Bz_2O_2
25	-	5000	-	0.24
40	650	1450	1.79	0.82
60	120	250	9.23	4.40
80	28	60	37.50	17.50

Variations in Methods used for reporting Molecular Weight

Initially it was planned to report molecular weights as the number average molecular weight $\overline{Mn}$ obtained from Osmometry as described in Chapter 2 and the weight average molecular weight derived from viscosity results. Using the generally accepted Mark Houwink equation

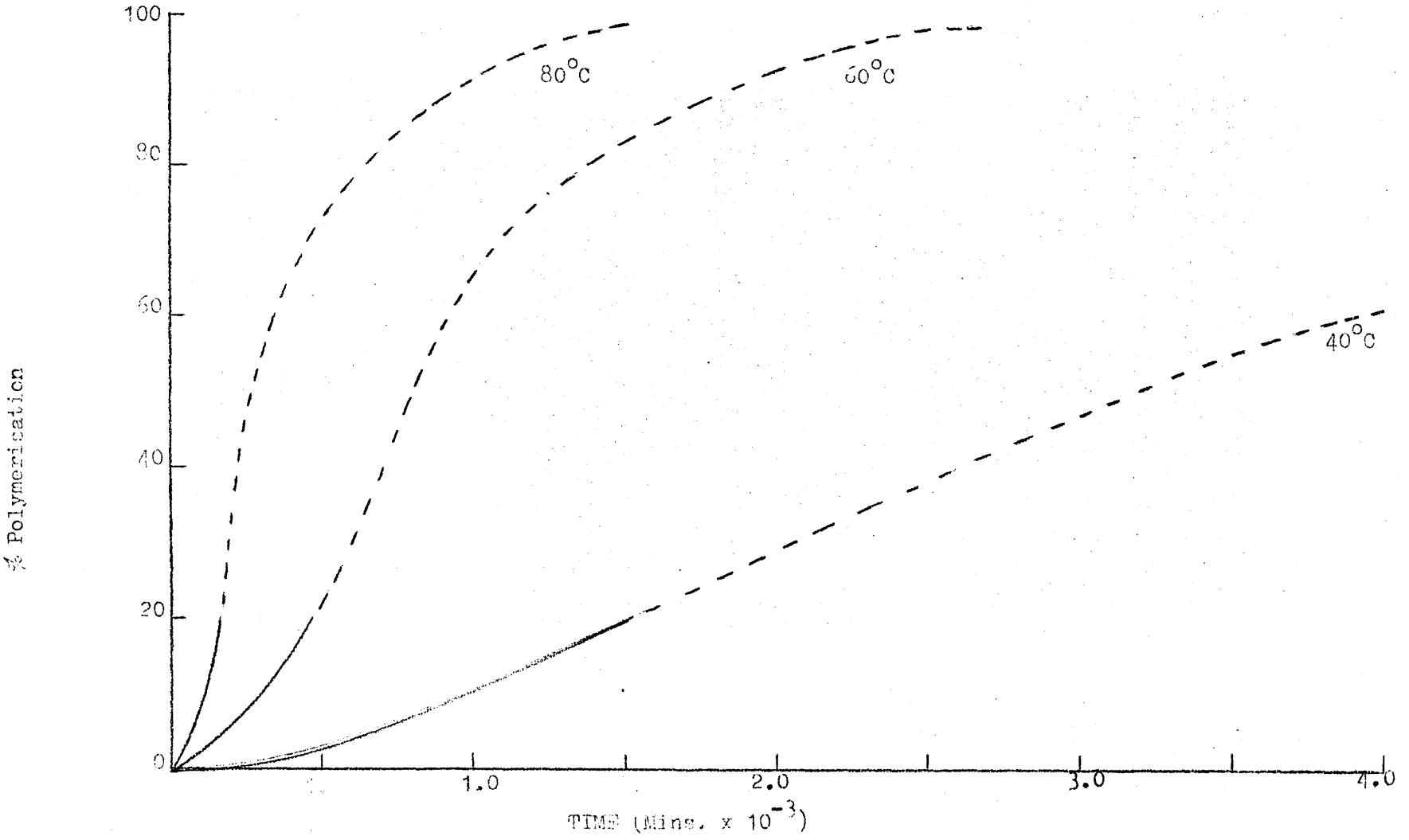


Fig. 3-6 BULK POLYMERISATION OF VINYL CHLORIDE AT 40, 60 and 80°C using 0.01 M% AIBN
(Solid line : Dilatometric conversion measurements
Dashed line: Gravimetric conversion measurements)

$$[\eta] = KM^{\alpha}$$

where K and α are constants for a particular system and $[\eta]$ is the intrinsic viscosity of the polymer in solution.

The constants K and α are experimentally determined by absolute methods of determination of molecular weight and are to be found in the literature and polymer hand books.

Depending on the method of determining K and α will determine whether the viscosity method of molecular weight determination will result in number or weight - average values. Initially we used the figures of Mead and Fuoss[143] of $K = 1.1 \times 10^{-5}$ d l/g and $\alpha = 1$ for cyclohexanone PVC system at 25°C, however, on comparing more recent figures for K and α it was found that the range could be quite wide as shown in Table 3-2 and 3-3.

In figure 3-7 the values of $\bar{M}w$ derived from 3 different sets of K and α values are plotted against $[\eta]$

Table 3-2. K and α values for derivation of $\bar{M}n$ through viscosity measurements

$K \times 10^5$ ($d\ g^{-1}$)	α	Temperature °C	Method Used	Ref.
11.6	0.85	20	Osmometry	123
13.7	1.00	20	"	124
112.5	0.63	20	"	124
12.3	0.87	25	"	125
24.0	0.77	25	"	126
204.0	0.56	25	"	127

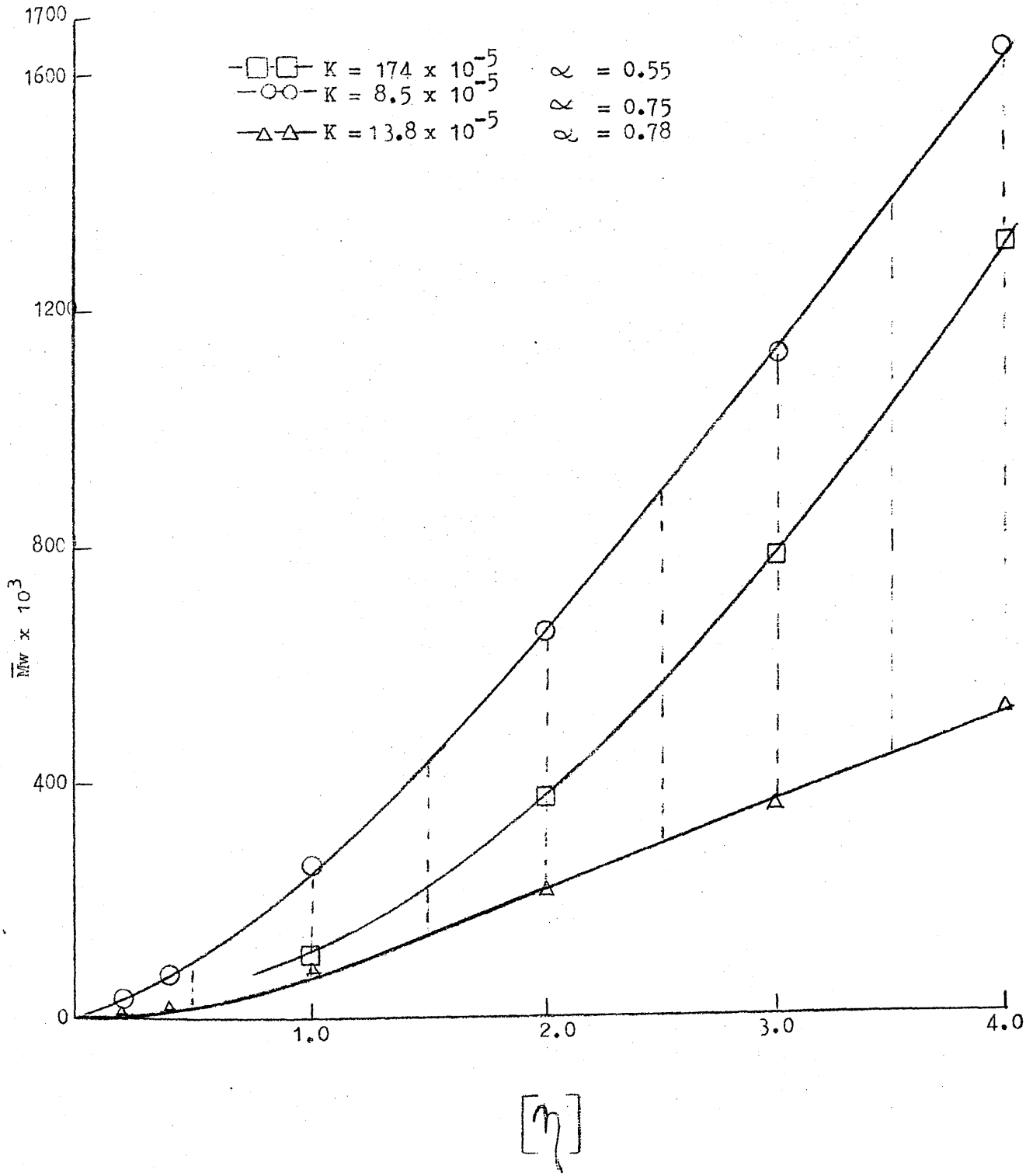


Fig. 3-7 $\bar{M}w$ CONVERSIONS USING DIFFERENT K AND α VALUES

Table 3-3. K and α value for derivation of $\bar{M}w$ through viscosity measurements.

$Kx\ 10^5$ ($d\ g^{-1}$)	α	Temperature °C	Method	Ref.
174.0	0.55	25	Light Scattering	128
8.5	0.75	25	"	129
13.8	0.78	25	"	130

From this plot it will be seen that a polymer with an $[\eta]$ value of 0.67 may have a value of $\bar{M}w$ between 50.8×10^3 to 152.3×10^3.

Due to this variation we have elected to report our results in both intrinsic viscosity values $[\eta]$ and $\bar{M}n$ derived from osmometry.

From our osmometry results we plotted $\log \bar{M}n$ against $\log [\eta]$ and derived a new value of $K = 29 \times 10^{-5}$ and $\alpha = 0.72$ which compares closely to the value of $K = 24 \times 10^{-5}$ and $\alpha = 0.77$ as reported Danusso et al[126].

Effect of Initiator type and Concentration on Molecular Weight

Table 3-4 shows the variation in $[\eta]$ and $\bar{M}n$ with concentration of AIBN and Bz_2O_2 at approximately 80% conversion when polymerised at 60°C. For both the AIBN and Bz_2O_2 initiated polymerisations there is a decrease in $[\eta]$ and $\bar{M}n$ with increase in initiator concentration. There is also a slight difference in the values of $[\eta]$ and $\bar{M}n$ for the two initiators at the same concentration. The average rate of polymerisation was also shown, earlier, to differ for AIBN and Bz_2O_2.

Table 3-4. The effect of type of initiator, AIBN and Bz_2O_2 on molecular weight of PVC at different concentrations 0.01, 0.10 and 1.0 Mole % polymerised at 60°C for about 80% polymer conversion

Initiator	Initiator Concentration M%	High Polymerisation % Conversion	$[\eta]$	$\bar{M}n \times 10^3$
Bz_2O_2	0.01	80.8	0.87	71.9
	0.10	72.0	0.71	61.5
	1.0	83.2	0.69	51.0
AIBN	0.01	78.0	0.84	82.5
	0.10	78.5	0.79	62.8
	1.0	79.1	0.76	54.9
		Low Polymerisation % Conversion		
Bz_2O_2	0.01	4.34	0.65	67.1
	0.10	7.02	0.56	45.4
	1.0	4.83	0.47	37.2
AIBN	0.01	4.0	0.73	57.2
	0.10	4.26	0.70	54.0
	1.0	5.30	0.65	49.1

Table 3-5 The effect of initiator type at high temperature (120°C) polymerisation, on molecular weight

Initiator Type 0.10 M %	% Conversion	$[\eta]$	$\overline{Mn} \times 10^3$
AIBN	4.78	0.25	17.4
Bz O_2	2.78	0.11	15.8

The difference being greatest 71.9 x 10^3 and 82.5 x 10^3 in the case of the lowest initiator concentration and almost identical in the case of the other initiator concentration.

The same effect is detected for the high temperature polymerisations at 120°C, although in this case the polymer conversion is between 2 and 5%. Table 3-5.

For low % conversions of around 5% (Table 3-4) the difference in the value of $[\eta]$ for the same initiator concentration, is significant, and in all cases is higher for AIBN. The difference being greater by 12, 25 and 38% for 0.01, 0.1 and 1.0 Mole % respectively. $\overline{Mn}$ is higher for AIBN in two cases,
54 x 10^3 and 49.1 x 10^3 for 0.1 and 1.0 Mole % respectively, and reverses itself for 0.01 Mole % being 57.2 x 10^3 as opposed to 67.1 x 10^2 for Bz_2O_2.

The above results are rather surprising in view of the fact that the rate of polymerisation, is greater with AIBN than Bz_2O_2. Possibly chain transfer to initiator may occur with Bz_2O_2 and this may be responsible for the slight differences in molecular weight.

The effect of benzoyl peroxide concentration on the molecular weight of the polymer in polymerisations at 60°C is also shown in

Table 3-4. An increase in the value of $[\eta]$ from 0.69, 0.71 and 0.87 occured (i.e. a difference of 26%) with decrease in the initiator concentration from 1.0, 0.10 and 0.01 Mole % respectively.

$\bar{M}n$ showed the same effect increasing from 51.0×10^3 to 71.9×10^3 with decreasing initiator concentration a difference of almost 40%. For AIBN the same phenomena occurs, however, the increase in $[\eta]$ is not as marked, only, 11%. In the case of $\bar{M}n$ which shows the same trend, the difference is slightly greater than for Bz_2O_2, a difference of about 51%. It appears that increases in the initiator concentration result in polymers of lower molecular weight being formed. However, the relationship between initiator concentration and molecular weight is not a direct one, indicating that chain transfer reactions, probably, play a role in the determination of the molecular weight of the polymer.

Effect of Polymerisation Temperature on Molecular Weight

In the temperature range of 25°C to 80°C at an initiator concentration of 0.01 Mole % Bz O_2 for polymers in the range of 80% conversion $[\eta]$ drops markedly from 2.6 for 25°C to 0.5 for 80° C a five fold drop. $\bar{M}n$ values also drop from 175.1×10^3 to 30.4×10^3 almost a 6 fold drop for the same temperature range as reported in Table 3-6.

For low polymer conversions in the range of 5% table 3-7 the same occurs with a slightly bigger 6.5 fold drop in $[\eta]$ than for the above high conversion polymers for the same temperature range.

The same trend is observed for the high temperatures reaching a low $\bar{M}n$ of 15800 for the 120° C polymerisations Table 3-8. However at these high temperatures one cannot be sure of either the mechanism or the conditions of the reaction especially whether degradation has been already initiated. These polymers will be therefore used

Table 3-6 The effect of polymerisation temperature on the molecular weight of polyvinyl chloride polymerised with 0.01 M% Bz_2O_2.

Polymerisation Temperature °C	% Conversion	$[\eta]$	$\bar{M}n \times 10^3$
25	80.0	2.6	175.1
40	84.0	1.5	139.0
60	80.8	0.9	71.9
80	78.0	0.5	30.4

Table 3-7 The effect of polymerisation temperature on the molecular weight of low conversion polyvinyl chloride polymerised with 0.01 Bz_2O_2

Polymerisation Temperature °C	% Conversion	$[\eta]$
25	4.2	2.17
40	6.7	1.13
60	4.3	0.65
80	5.2	0.33

only as a curiosity item in our work rather than a base for our study.

At the other end of the temperature range (0°C to - 75°C) some photoinitiated polymerisations using 0.01 M% - AIBN initiator were carried out.

This gave some relatively high molecular weight polymer covering the range of $[\eta]$ 2.2 to 3.6 with a levelling off at - 25°C as reported by others. The results are shown in Table 3-9. The value of 3.6 for $[\eta]$ at - 50°C is about four times that of an equivalent polymer made at 60°C.

Table 3-8 The effect of high temperature of polymerisation of polyvinyl chloride using 0.1 M % Bz_2O_2

Polymerisation Temperature °C	% Conversion	$[\eta]$	Mn x 10^3
100	28.3	0.15	17.4
	72.5	0.30	37.2
120	2.8	-	15.8
	26.6	0.14	-
140	17.8	0.09	-

Table 3-9 The effect of low temperature Photo polymerisation on polyvinyl chloride using 0.01 M % AIBN

Polymerisation Temperature °C	Conversion %	$[\eta]$
0	20.3	2.2
-25	22.2	3.5
-50	19.6	3.6
-75	18.0	Insoluble

Effect of Conversion on Molecular Weight

The effect of conversion was studied using both Bz_2O_2 and AIBN initiator over a wide temperature range as well as three different initiator concentrations, which will be further discussed in the degradation section. At 60°C and 0.1 Mole % Bz_2O_2 we obtained a decrease in $[\eta]$ values with increased % conversion, the difference over a range of 7.0 to 72% conversion is about 27% . This also reflects itself in the $\bar{M}n$ values (table 3-10)

The same phenomena occurs with AIBN under the same conditions (table 3-11) with a slightly smaller difference in $[\eta]$: 17% for a wider % conversion range of 4.3% to 95.5%

Table 3-10 The effect of conversion on the molecular weight of polyvinyl chloride polymerised at 60°C with 0.1 Mole % Benzoyl peroxide

% Conversion	$[\eta]$	$\overline{Mn} \times 10^3$
7.0	0.56	45.4
19.5	0.61	48.5
41.8	0.67	54.0
57.0	0.70	58.5
72.0	0.71	61.5

Table 3-11 The effect of conversion on the molecular weight of polyvinyl chloride polymerised at 60°C with 0.1 Mole % AIBN

% Conversion	$[\eta]$	$\overline{Mn} \times 10^3$
4.3	0.70	54.0
10.9	0.72	54.5
37.0	0.74	57.0
60.5	0.79	60.0
95.5	0.82	64.5

Determination of the Chain Transfer to Monomer

By plotting the reciprocal of the degree of polymerisation $\frac{1}{DP}$ against the square root of initiator concentration the chain transfer constant C_{tr} was obtained figure 3-8. The value obtained for AIBN was 1.1×10^{-3} amd 1.0×10^{-3} for Bz_2O_2. As can be seen from the graph the slope for AIBN is almost flat indicating that that chain transfer to monomer is slightly more significant than for Bz_2O_2. It is also

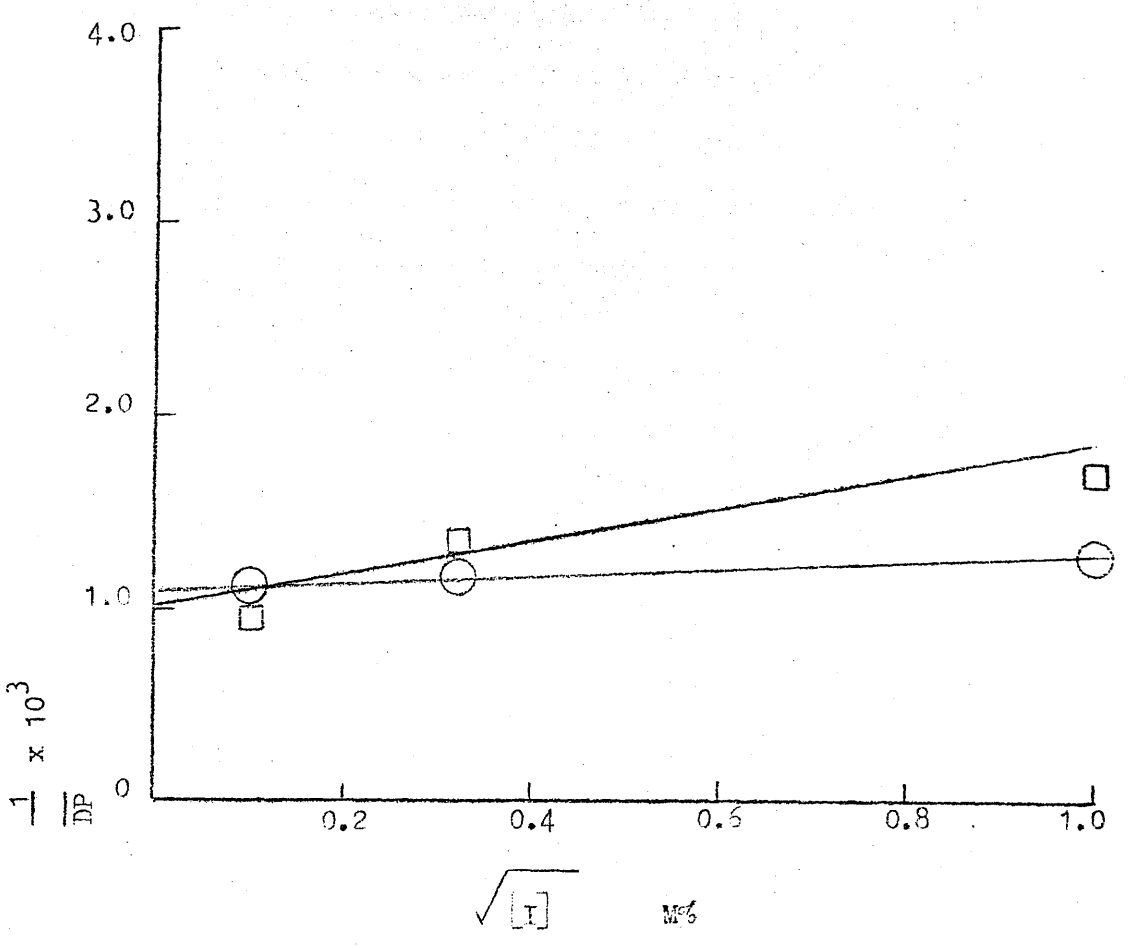


Fig. 3-8 DEGREE OF POLYMERISATION AS EFFECTED BY INITIATOR CONCENTRATION

Bz_2O_2 —□—□— AIBN —○—○— for 5% conver.

evident that the points for B_2O_2 do not perfectly fit a straight line indicating the lack of a direct relation between the reciprocal of the degree of polymerisation and the rate. This may probably be due to other competing reactions such as, transfer to initiator.

An approximate estimate of the activation energy for chain transfer was also determined by plotting $\ln \frac{1}{[\eta]}$ against $\frac{1}{TA^{\circ}}$ and determining the slope, fig. 3-9. The value obtained for Bz_2O_2 peroxide initiated polymerisation at 5% conversion is 16.4

From this limited work it is obvious that the chain transfer to monomer is an important reaction in the polymerisation of vinyl chloride. The fact that temperature has a greater effect on DP than does initiator concentration supports this view.

Molecular Weight Distribution

In an attempt to obtain an indication of molecular weight distribution and hence branching and other such irregularities, British Petroleum agreed to conduct a limited series of Gel Permeation determinations. These values unfortunately will have to be viewed within their limited context, since as was mentioned earlier, molecular weight determination techniques are biased techniques and hence relative in nature.

Effect of polymer conversion on Molecular Weight Distribution

Their results confirmed a change in molecular weight with conversion, however, the trend is in the reverse direction to what was previously found using viscometry i.e. their results indicate a decrease in both $\overline{Mw}$ and $\overline{Mn}$ with increase in conversions for both 0.01 M % Bz_2O_2 initiated polymers, table 3-12 and 0.01 M % AIBN initiated polymers table 3-13, both at 60°C polymerisation temperature.

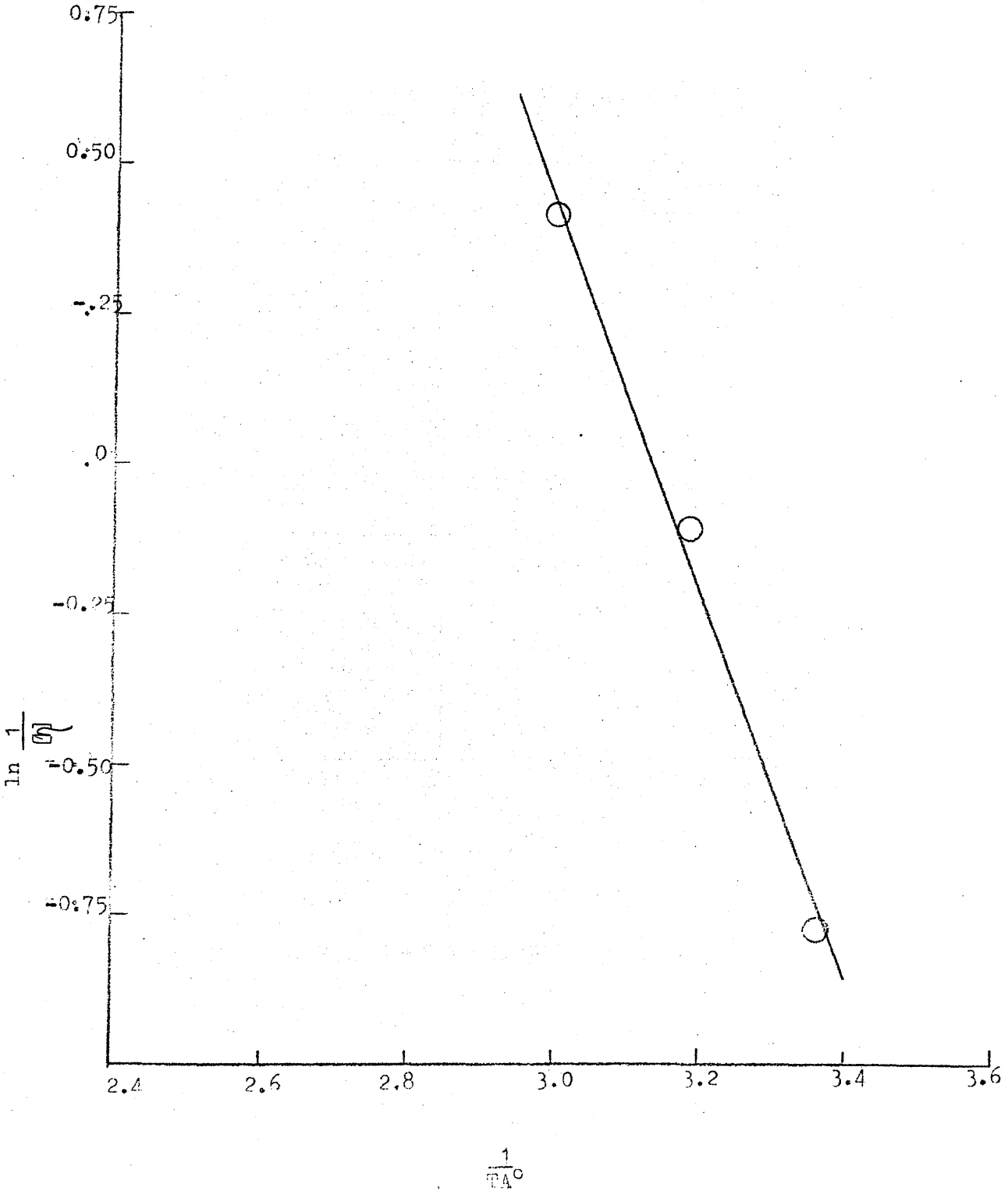


Fig. 3-9 EFFECT OF $\frac{1}{TA^{\circ}}$ on $\log\frac{1}{[\eta]}$ FOR DETERMINING ACTIVATION ENERGY OF TRANSFER TO MONOMER REACTION

The difference is slightly more marked for AIBN.

The distribution ratio was found to be in the range of 2.04 to 2.16 for AIBN for a conversion range of 4 to 78% and 2.06 to 2.16 for Bz_2O_2 initiated polymers for the almost same conversion range.

Table 3-12 The effect of polymer conversion on molecular weight distribution for AIBN (0.01 M%) initiated PVC at 60 °C.

% Conversion	$\overline{Mw} \times 10^3$	$\overline{Mn} \times 10^3$	$\overline{Mw}/\overline{Mn}$
4.0	67.1	32.9	2.04
67.0	80.4	37.2	2.16
78.0	82.5	39.4	2.09

Table 3-13 The effect of polymer conversion on molecular weight distribution for Bz O_2 (0.01 M%) initiated PVC at 60°C.

% Conversion	$\overline{Mw} \times 10^3$	$\overline{Mn} \times 10^3$	$\overline{Mw}/\overline{Mn}$
4.0	65.2	31.6	2.06
65.0	72.6	34.9	2.08
81.0	79.9	37.1	2.16

A value of 2 would be expected for the polymerisation of a vinyl monomer in which the molecular weight is controlled by chain transfer to monomer or termination by disproportion.

Effect of Initiator type and concentration on molecular weight distribution

The results obtained for $\overline{Mw}$ and $\overline{Mw}/\overline{Mn}$ for 0.01 and 0.10 M % Bz_2O_2 are shown in table 3-14 and confirm our intrinsic viscosity findings of a decrease in molecular weight with an increase in initiator concentration, except in the low conversion polymers where the trend is reversed.

The increase is most marked for polymer which has been taken to about 60°C conversion.

Table 3-14 The effect of Bz_2O_2 initiator concentration on molecular weight distribution of PVC polymerised at 60°C on different conversions.

Mole % Bz O_2	Conversion	$\overline{Mw} \times 10^3$	$\overline{Mn} \times 10^3$	$\overline{Mw}/\overline{Mn}$
For Low Conversions				
0.01	4.34	65.2	31.6	2.06
0.10	7.02	94.7	47.0	2.01
For Medium Conversions				
0.01	65.5	72.6	34.9	2.08
0.10	57	67.0	29.9	2.42
For High Conversions				
0.01	80.8	79.9	37.1	2.16
0.10	90.0	67.4	30.1	2.24

A comparison of the polymer formed using AIBN and Bz_2O_2 as initiator is given in table 3-15.

In all three cases $\overline{Mw}$ is greater for 0.01 M% AIBN initiated polymers which coincide in general with our findings.

The $\overline{Mw}/\overline{Mn}$ ratio is almost identical for low conversions, however for medium conversions Bz_2O_2 has a lower ratio than AIBN, and a higher ratio at 80.8% conversion. The highest ratio is 2.16 indicating, relatively within this series, the highest degree of branching for 0.01 M % Bz O_2 initiated polymer at 80% conversion.

Effect of polymerisation temperature on Molecular weight distribution

The results as shown in table 3-16 show a definite trend of increasing $\overline{Mn}$ and $\overline{Mw}$ with decrease in temperature of polymerisation and an increase in $\overline{Mw}/\overline{Mn}$ ratio with decrease in polymerisation temperature indicating less branching and less probability of forming

greater stereoregularity. The figure of 8.7 for the 25°C polymerisation is doubtful however.

Table 3-15 The effect of type of initiator (AIBN vs Bz O_2) 0.01 M % on molecular weight distribution of PVC polymerised at 60°C.

For low conversions

Type of Initiator	% Conversion	$\bar{M}w \times 10^3$	$\bar{M}n \times 10^3$	$\bar{M}w/\bar{M}n$
Low Conversions				
Bz O_2	4.34	65.2	31.6	2.06
AIBN	4.0	67.1	32.9	2.04
For Medium Conversions				
Bz O_2	65.5	72.6	34.9	2.08
AIBN	67.0	80.4	37.2	2.16
For High Conversions				
Bz O_2	80.8	79.9	37.1	2.16
AIBN	78.0	82.5	39.4	2.09

Table 3-16 The Effect of polymerisation temperature on 0.01 M% Bz_2O_2 initiated PVC.

Polymerisation Temperature °C	% Conversion	$\overline{Mn} \times 10^3$	$\overline{Mw} \times 10^3$	$\overline{Mw}/\overline{Mn}$
80	52.0	19.9	39.4	1.98
60	65.5	34.9	72.6	2.08
40	55.0	62.7	179.5	2.86
25	53.0	93.3	812.1	8.70

Solution polymerisations

A cursory study was performed on the thermal polymerisation of vinyl chloride at 60°C in the presence of solvents or diluents using 0.01 M % of radioactive Bz_2O_2. A 1 : 1 monomer to liquid volume ratio was maintained throughout. The purpose of the study was to empirically

scan as many liquids as practical for phenomenal effect on dehydrochlorination to try and detect effects of solvent transfer (especially the introduction of chain end extraneous groups), to determine the different effects of solvents, precipitants plasticisers with different functional groups on the polymerisation reaction and the effect of hetrogeneity and lastly to hopefully detect one or two interesting systems for more detailed study.

The solvents used were selected to represent the following groups: hydrocarbons esters, halogens, ethers, ketones, amines, amides and nitrocompounds. Table 3-17 gives the breakdown of solvents used, the rate of polymerisation and viscosities.

Table 3-18, 3-19 and 3-20 show the same information for non - PVC solvents, plasticisers and stabilisers respectively. There seems to be a correlation between the solubility affinity of the different solvents to PVC and the rate at which the polymers are formed. The rate of polymerisation increases in the following order; ethyl benzoate, < benzophenone, < cyclohexanone, < chlorobenzene, < bromobenzene, < methyl iodide, < dimethylformamide, < tetrahydrofuran, < dichlorobutane and < dimethylacetamide.

Table 3-17. Data on solution polymerisation at 60°C using 0.01 M % Bz_2O_2 at 1 : 1 Monomer : Solvent volume ratio.

Solvent	% Conversion		Rate (moles l^{-1} s^{-1} at 20% Conversion x 10^5	$[\eta]$	Comments
	%	Hrs.			
ethylbenzoate	3.8	6	1.8	0.45	White gel formed
	21.7	42		0.48	
cyclohexanone	6.8	6	2.7	0.25	Viscous yellow liquid
	25.6	42		0.19	
benzophenone	1.6	6	2.5	0.24	Polymer precipitated
	44.5	42		0.26	
tetrahydrofuran	16.7	6	8.6	0.12	White gel formed
	54.6	42		0.17	
dimethylformamide	14.8	6	7.3	0.22	A violet gel formed
	50.7	42		0.25	
dimethylacetamide	22.9	6	13.4	0.25	Violet gel formed
	31.4	42		0.27	
dichlorobutane	21.8	6	12.3	0.43	White gel formed
	78.5	42		0.47	
chlorobenzene	6.4	6	3.2	0.42	White gel formed
	35.9	42		0.42	
bromobenzene	7.4	6	3.5	0.39	Clear gel formed
	39.4	42		0.39	
methyl iodide	12.1	6	6.4	0.20	Clear gel formed
	64.2	42		0.23	

Table 3-18. Data on solution polymerisation using poor PVC solvents at 60°C and 0.01 M % Bz_2O_2 at 1 : 1 monomer : solvent ratio

Solvent	Conversion %	Conversion Hrs.	Rate x 10^5 Moles l^{-1} s^{-1} (at 20% Conversion)	$[\eta]$	Comments
cyclohexane	12.2	6	6.4	0.39	
isopropylbenzene	2.3	6	2.9	0.15	precipitated polymer
	15.1	42		0.16	
nitrobenzene	—		—	—	discoloured to dark brown
benzylalcohol	2.2	6	0.8	—	viscous liquid
	9.0	42			
dichloronaphthalene	0.02	6	0.0	—	white solid formed
	0.35	42			
hyridene	0.23		—	—	No polymer. Yellow brown colour formed

Table 3-19 Data on solution polymerisation using plasticisers at 60°C and 0.01 M % Bz O_2 at 1 : 1 monomer : solvent volume ratio.

Solvent	Conversion %	Conversion Hrs.	Rate x 10^5 moles l^{-1} s^{-1} (at 20% Conversion)	$[\eta]$	Comments
tritolylphthalate	5.5	6	2.2	0.25	A gold gel formed
	23.5	42		—	
dioctylphthalate	10.4	6	7.0	0.44	White gel formed
	62.3	42		0.48	
dibutylphthalate	10.8	6	4.5	0.47	Clear gel formed
	60.00	42		0.51	

Table 3-20. Data on solution polymerisation using commercial stabilisers at 60°C and 0.01 M % Bz_2O_2 at 1 : 1 monomer : solvent ratio by volume

Solvent	Conversion %	Conversion Hrs.	Rate x 10^5 Moles l^{-1} s^{-1} (at 20% Conversion)	$[\eta]$	Comments
tridec y lphosphite					No change
	0.1	42	——	——	No polymer joined
diethyl phosphate	7.8	6	4.5	——	White gel
	51.9	42			
epoxyoctyltallate	9.0	6	3.2	0.30	Solid white polymer joined
	36.4	42		0.33	
Mellite	0.2	6	——	——	
Vinco	0	6	——	——	No reaction

Dimethylacetamide and dichlorobutane stand in a class of their own with an average rate around 13 x 10^{-5} compared with an average rate of about 2 x 10^{-5} for a group consisting of ethyl benzoate, cyclohexanone and benzophenone. However, due to either inhibition or degradative chain transfer reactions the highest % polymer conversion after 42 hrs. follows a different order; Dichlorobutane still is at the top with 78% followed by methyl iodide 64% followed by dimethyl formamide and tetrahydrofuran at about 50%.

The intrinsic viscosities with conversion does not vary that much with few exceptions. These exceptions are for tetrahydrofuran where the change is about 42% and for cyclohexanone with a 24% drop from 6 to 25% conversion. Tetrahydrofuran is known to be an effective transfer agent.

The highest molecular weights were obtained with dichlorobutane, ethyl benzoate and chlorobenzene with the lowest molecular weights for

tetrahydrofurane. The difference between the highest and lowest being a factor of 3.75.

Of interest also is the formation of colour in the case of both dimethyl formamide and dimethyl acetamide and a yellow colour with cyclohexanone.

All of the polymers in this category except benzophenone, which probably belongs to the poor solvent category, formed gels and remained in solution rather than precipitating out. In the case of poor PVC solvents the only appreciable rates obtained were those for cyclohexane and isopropylbenzene at 6.42×10^{-5} and 2.89×10^{-5} moles $l^{-1}s^{-1}$ respectively. Again, we noticed some discolouration even in the absence of polymer, probably due to the liberation of free radicals and decomposition, of solvents.

In case of polymerisation in presence of plasticisers dioctyl phthalate had fastest rate 7.03×10^{-5} as compared to 4.48 and 2.24 for dibutyl pthalate and diactyl phthalate respectively. The rate of 7.03×10^{-5} compares with that obtained with dimethylformamide in the solvents series.

The intrinsic viscosities indicate a high molecular weight for both dioctyl and dibutyl phthalates of .44 to 0.51 and a low $[\eta]$ for tritolyl phthalate of 0.25.

There seems to be an increase in viscosity with conversion and all polymers remained in solution.

In this case the rate of conversion at 20% polymerisation follows the same order as the rate after 42 hrs. and follows the descending order dioctyl phthalate 62%, dibutyl pthalate 60% and tritolyl phthalate 23%, still the big difference in average rate at 20% conversion of 7.03×10^{-5} and 4.48×10^{-5} does not manifest itself in the final %

yield for dioctyl and dibutyl phthalate respectively.

For Polymerisation in presence of PVC commercial stabiliser table 3-20; the only two reactions that materialised were with diethyl phosphate with an average initial rate of 4.47×10^{-5} and going to 52% conversion, and with the epoxyoctyltallate giving us an average initial rate of 3.2×10^{-5} and 36% conversion with an $[\eta]$ of 0.33.

Discussion

The degree of polymerisation, $\overline{DP}$ is defined as the average number of monomer units in the polymer molecule formed in the reaction, hence there is a direct relationship between the degree of polymerisation and the molecular weight of the polymer. The molecular weight of the polymer increasing as the rate of propagation increases and decreasing as the rates of termination and chain transfer increases.

Heterogeneous polymerisation processes do not obey the ideal kinetic scheme outlined in the introduction. Therefore, changes in molecular weights of polymers made by such processes can only be discussed in terms of the relative importance of the propagation, termination and chain transfer reactions.

The molecular weight of PVC has been found to be independent of the extent of conversion to polymer and the initiator concentration by Bengough and Norrish[11] and Schindler and Brietenbach[12] and they concluded that chain transfer to monomer essentially determined the $\overline{M}w$. of the polymer. Chain transfer to initiator is also reported to be an important reaction affecting the molecular weight[13].

The above view was supported by Danusso and Sianesi[14] who found the constant for chain transfer to monomer for the bulk polymerisation

of vinyl chloride at 60°C to be 1.48×10^{-3}. In a more recent paper Talamini and Vidotto[15] analysed the molecular weight distribution curves of various PVC samples prepared under different conditions and concluded, in disagreement with previous work, that chain transfer to monomer does not play a very important role in vinyl chloride polymerisation. The disagreement between the results of the various workers may be because the equation for the determination of the chain transfer constant is strictly valid only for homogeneous polymerisation.

The anomalous effect of the polymerisation temperature on the molecular weight of PVC was also found by us which coincides with what Talamini and Vidotte reported earlier[16]. The molecular weight of the polymer increases with decreasing polymerisation temperature reaching a steady plateau value at - 30°C. A similar effect was observed in the heterogeneous bulk polymerisation of acrylonitrile where the maximum was found to occur at 60°C[17]. This behaviour was thought to have been caused by the occlusion of the chain radicals in the polymer particles. At temperatures above 60°C, the occlusion is so reduced that bimolecular termination becomes unrestricted and the molecular weight begins to fall while the propagation rate constant increases while termination will remain unaltered with increasing temperature. It might be expected, therefore, that there should be a maximum in the curve of molecular weight against temperature for all heterogeneous polymerisations. Tallamini and Vidotto[18] also suggested in a later report that the maximum in molecular weights is not only due to temperature variations affecting occlusion of polymer radicals but may also be due to structural changes in the polymer causing changes in the degree of swelling of the polymer particles and the increase in its stereoregularity with the decrease in polymerisation

temperatures as confirmed by X-ray data. It is also possible, however, that the effect may merely be the result of more effective chain transfer reactions at higher temperatures resulting in a more effective control of molecular weight.

It is felt that both of the previous phenomena occur simultaneously which does not simplify matters. The molecular weight was found to be slightly dependent on initiator concentration, decreasing with an increase in initiator concentration. This is somewhat similar to the findings of Arlman and Wagner[23] and also provides the argument that chain transfer is the controlling factor in determining the molecular weights of the resultant polymers. Another influence could be the deviation from isothermal reaction condition with increase in initiator concentration. Bengough[24] calculated the adiabatic increase in the polymerisation temperature for vinylacetate and reported a rise of temperature of about 1.5×10^{-3} °C per second. This, however, was at high temperatures and at the high end of initiator concentration. This explanation also fits well with the previous relation of molecular weight dependence on polymerisation temperature.

The effect of the presence of solvents for PVC such as THF, 1-2 dichlorethane and chlorobenzene on molecular weight have been reported[19]. The presence of a solvent for the monomer but not the polymer, such as cyclohexane has also been found to effect the molecular weight of the polymer[20].

THF was found to be a very active chain transfer agent. Dichloralthane is less effective as a chain transfer agent with a peculiar molecular weight versus monomer concentration relation showing two maximas. The molecular weights of the polymers formed in chlorobenzene indicate copolymerisation occuring[21].

These are only some of the anomilies of solution polymerisation, it is evident that there has not been much work reported in this area. From our empirical and cursory studies in this area, we are convinced that there is a lot to be learned from pursuing this route.

CHAPTER 4

THERMAL STABILITY OF PVC

At room temperature PVC is inherently stable. Increase in temperature to above 100°C leads to decomposition with evolution of hydrogen chloride (HCl) and development of colour in the polymer.

As the bond strength of the C-Cl bond is of the order of 80 K cal $mole^{-1}$ the hypothetical head-to-tail structure for PVC is not likely to lose HCl below 300°C. It is assumed, therefore, that there must be labile structures, within the polymer, which are responsible for these decomposition reactions. Being aware of the instability of PVC relative to saturated alkyl chlorides and the reactivity of organic compounds with allylic structures, early workers proposed that HCl was lost primarily from sites where special lability was imparted to chlorine atoms by reason of their location relative to double bonds. It has since been shown that it is the initiation step which holds the key to the mechanism of dehydrochlorination and that degradation can be initiated from several structural abnormalities in the polymer, as discussed in Chapter 1. The main structural imperfections which may affect the initiation of dehydrochlorination are initiator fragments, unsaturated end groups, branch points, random unsaturation within the chain, traces of oxygen, head-to-head units and sequences of stereoregularity.

Although much work has been undertaken no conclusive evidence exists as to which is the major cause of the initiation of degradation. Consequently, this work has been undertaken in an effort to produce PVC under various but controlled polymerisation conditions with a

view of minimising the above imperfectations and also attaining an improved base for relative comparison.

Effect of Polymerisation Conditions on the Structure of PVC. Vinyl chloride is a relatively unreactive monomer which under certain conditions responds to free radical initiators to form a high polymer. The end result of the polymerisation process is high molecular weight PVC which is fairly uniform in a chemical sense, but may contain a variety of molecular weight species, many of which possess a range of structural abnormalities within the chain. The presence of these structural imperfections may be considered as being a direct result of the reactions undergone during the polymerisation process. Consequently, it is believed that by strict control of the polymerisation conditions, it is possible to reduce and possibly remove many of these irregularities of the polymer chain. The polymers produced in this study are the result of free radical polymerisation reactions which have been carried out under conditions of high vacuum with Bz_2O_2 and AIBN as initiators. Thus, every effort has been made to prevent oxygen links from occurring within the polymer chain, and any subsequent changes in the polymerisation conditions are unlikely to affect this. However, the presence of the other structures which give rise to instability within the polymer is believed to depend upon the polymerisation conditions. Consequently, any changes in the polymerisation conditions will affect the structure and thereby the thermal stability of PVC. The changes in polymerisation conditions studied have been.

Nature and Concentration of Initiator: The breakdown of free radical producing compounds such as benzoyl peroxide or AIBN in a polymerising system results in initiator fragments which react with monomer to form radicals capable of further addition of monomer to produce a polymer. Thus, for ideal polymerisation where there is no chain transfer, there will

be at least one, possibly two initiator fragments present in each chain. However, if chain transfer reactions are present there will be a number of polymer chains which will contain no initiator fragments. As the initiator concentration is altered the number of the radicals derived from the initiator and hence the rate of initiation must change accordingly. Consequently, there will be a different number of polymer chains formed, some of which will contain initiator fragments but many of which will not, depending on the amount of chain transfer present.

The nature of the initiator fragment will depend on the initiator used. In the majority of this work the initiator used was Bz_2O_2 and AIBN. Both initiators where C^{14} labelled and prepared in the Laboratory. The initiator fragment at the chain end, therefore will be a benzoyloxy phenyl group in the case of Bz_2O_2 and a cyanoisopropyl group for AIBN. Another difference is the decomposition by products of these two initiators, AIBN producing nitrogen and Bz_2O_2 producing carbon dioxide. Also unlike AIBN, Bz_2O_2 has the likliehood of further reaction with the polymer chain. Hence, only in the case of AIBN will changes in the polymer structure due to changes in the concentration of the initiator used occur at the polymer chain end.

Polymerisation Temperature: The temperature at which a monomer is polymerised affects most of the kinetic features of the process. The rates of each of the individual reactions and consequently the rate of overall polymerisation are temperature dependent. Changes in polymerisation temperature, therefore, result in changes of the kinetic features of the process and possibly may affect the structure of the polymer itself. As seen from the previous chapter, changes in the temperature of polymerisation of vinyl chloride cause changes in the molecular weight of PVC. The precise effect depends on the nature

of the polymerisation process as to whether it is carried out in bulk or in the presence of a solvent. Consequently the temperature of the polymerisation process may affect the type of termination process and the rate of the chain transfer reaction and therefore have a marked effect on the structure and thermal stability of the polymer itself. The amount of chain branching is also affected by changes in the polymerisation temperature. In most cases, the lower the polymerisation temperature, the lower the degree of branching and in general branching is not highly prevalent in PVC produced below room temperature[28]. Another effect of changes in polymerisation temperature is the changes which can occur in the crystallinity of the polymer. PVC is not generally classified as a crystalline polymer although, normally, there is a low degree of crystallinity present which is thought to be associated with syndiotactic sequences in the polymer.[131,132] It has been shown, however, that, as the polymerisation temperature is lowered, the degree of crystallinity of the polymer rises significantly and for a polymerisation temperature of $-75^{\circ}C$ the polymer formed is about 85% crystalline. These changes are thought to be due to the cumulative effect of a decrease in the degree of branching and an increase in the syndiotacticity of the polymer. Thus, it is likely that any changes which occur in the basic structure of PVC as a result of changes in polymerisation temperature below room temperature will appear within the chain and not at the chain end. Consequently, any changes in the thermal stability of PVC which result from altering the polymerisation temperature must be the result of structural changes within the polymer or be due to variations in the polymer molecular weight, and hence the number and the lengths of the polymer chains.

Extent of Polymer Conversion : As a polymerisation reaction proceeds and polymer is produced, it might be expected that the kinetics of the process might change. Chain transfer to polymer is one reaction which would be expected to become more important as the conversion increases. Some evidence of this is shown by the increase in the intrinsic viscosities of the polymers formed at higher conversions of monomer to polymer. This would seem to indicate that the degree of branching within the polymer chain is also somewhat dependent on conversion.

Presence of Solvents and Diluents : The bulk polymerisation of vinyl chloride is a heterogeneous process and hence the addition of a volume of solvent to the polymerising system can act in two ways depending on the nature and volume of the solvent added. The solvents used in this study, can be classified as solvents for both PVC and vinyl chloride and hence able to effect homogeneous polymerisation and solvents for the monomer but not the polymer and hence able to dilute the monomer which polymerises as if in bulk. One effect common to both systems is that the addition of solvent reduces the monomer concentration present, hence the rate of polymerisation, and possibly the molecular weight of the polymer formed. The presence of solvent also introduces the added complication of chain transfer to solvent reactions. These can have the effect of regulating the molecular weight of the polymer by terminating a growing polymer chain. If the chain transfer reactions are not of a degradative nature it is possible that the radicals derived from the solvent will reinitiate polymerisation. Consequently, many of the polymer chains will have solvent residues and not initiator fragments at their ends. Another important factor is that several solvents are known to undergo copolymerisation and it is

possible, therefore, that there will be some solvent fragments within the polymer chain. These fragments may vary in intrinsic stability and consequently may cause a variation in the rate of initiation of dehydrochlorination of PVC.

The presence of certain solvents during the polymerisation of vinyl chloride will affect the structure of the polymer chain. Solvents such as tetrahydrofuran, dimethylformamide and methyl iodide are very effective chain transfer agents and cause the molecular weight of the polymers produced to be drastically reduced. As a result, there are unlikely to be many chain transfer to polymer reactions, and hence, the degree of branching within the chains will be low. It has been suggested that certain other chain transfer agents, particularly aldehydes, exert an influence on the stereo-regularity of PVC prepared by free radical means[133-136]. It has been found that polymers produced in such a manner are highly crystalline and have molecular weights of less than 4,000.

Initiation by Irradiation : The decomposition of free radical producing catalysts is the generally accepted mode of initiation for a free radical polymerisation. The breakdown of the initiator may be achieved by the action of heat or other forms of energy such as ultra-violet or γ-radiation. The thermal decomposition of such initiators requires the polymerisation to be carried out at elevated temperatures whereas breakdown by irradiation enables the polymerisations to be performed at much lower temperatures. This will cause the degree of branching to be reduced to a minimum and produce a more crystalline polymer. The resultant polymer will still possess initiator fragments, although many of the other possible weak links within the chain will be removed. Thus, it might be expected that PVC produced in this manner would be more thermally stable provided that prolonged periods

of radiation have no harmful effect on the resultant polymer and that it is soluble enough for purposes of removing any unreacted initiator fragments.

RESULTS AND ANALYSIS

PVC that had been prepared under various polymerisation conditions, was precipitated, dried and then degraded in a manner as described in Chapter 2. The degradations were, whenever possible, carried out in a solution of ethylbenzoate under standard conditions of temperature ($198^{o}C$) and a carrier gas flow rate (14 litres $hour^{-1}$). The concentration of the polymer solution used for degradation purposes was 25 g $litre^{-1}$. Generally dehydrochlorination rates d(HCl)/dt are reported as total average rates (moles $l^{-1}s^{-1}g^{-1} \times 10^{7}$) and are based on degradation runs lasting 60 minutes, unless otherwise specified.

Dehydrochlorination Rate Characteristics.

Figure 4-1 and 4-2 show a typical titration run for the dehydrochlorination reaction of Bz_2O_2 and AIBN initiated PVC respectively. There are three basic features in most of the titration curves obtained. The first is the presence of an inhibition period which varies, in most cases, directly with the stability of the polymer. This is followed by a fast reaction rate R^1 ending with the third feature comprising of a slower rate R^2 as manifested by a sharp change in slope.

There could be two possible explanations for this specific profile of the titration curve.

1 - A chemical explanation based on two distinctively different degradation reactions which take place in sequence. The inhibition period would be somehow related to the energy level required for the

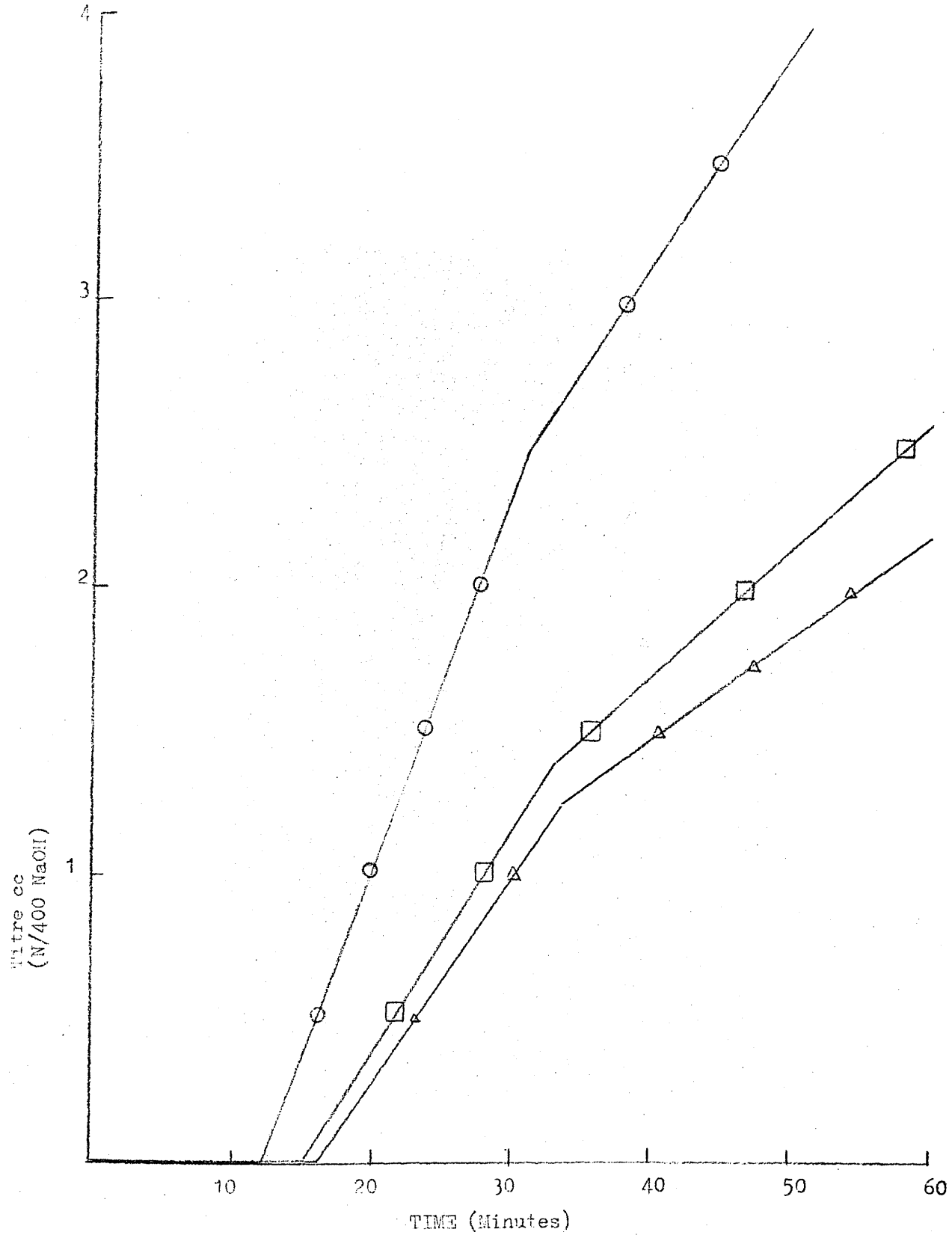


Fig. 4-1 REPRODUCTION OF TYPICAL TITRATION RUN
EFFECT OF INITIATOR (Bz_2O_2) CONCENTRATION ON THERMAL
STABILITY OF PVC POLYMERISED AT 60°C TO ABOUT 60% CONVERSION

—○—○— 1.0 M%
—□—□— 0.1 M%
—△—△— 0.01 M%

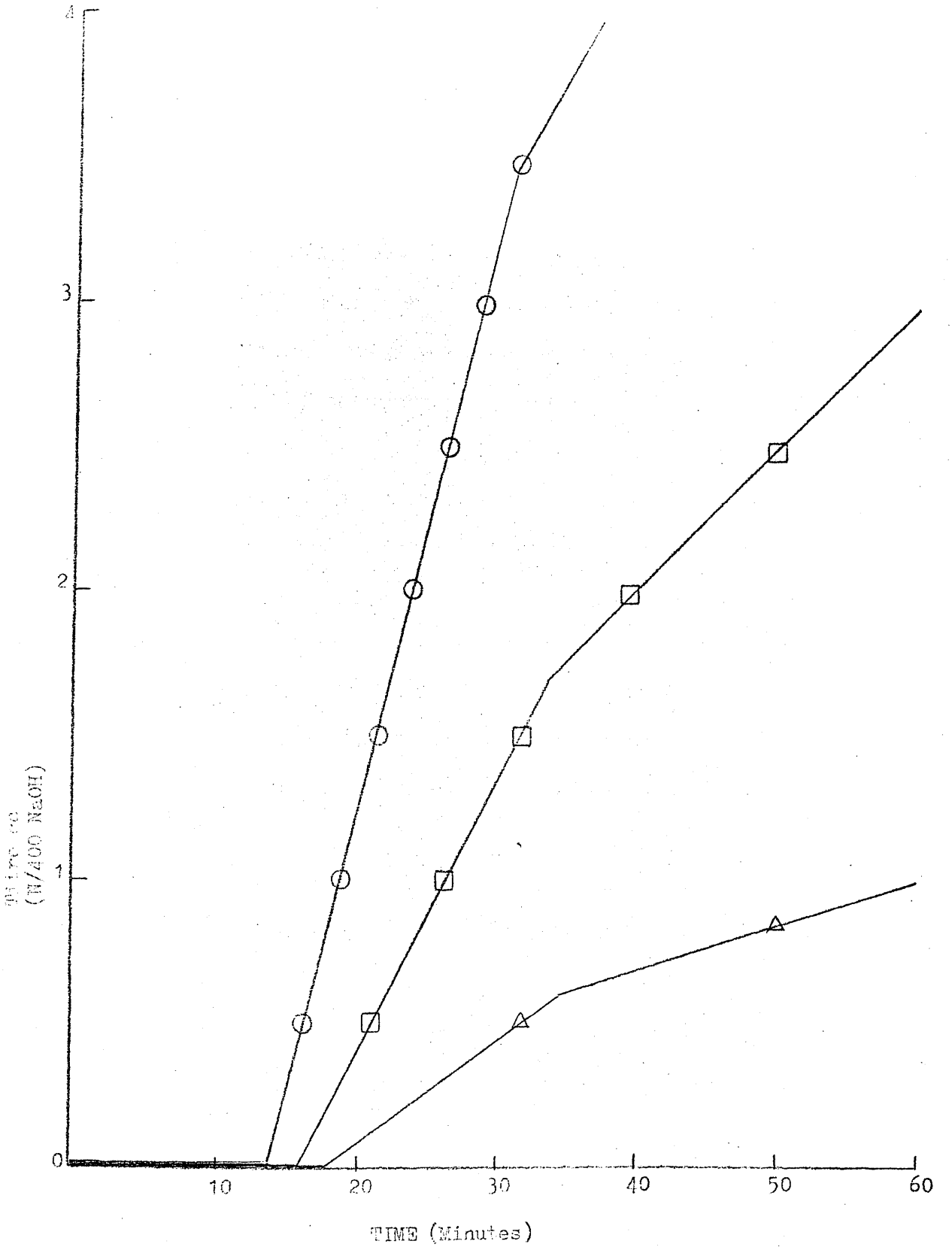


Fig. 4-2 REPRODUCTION OF TYPICAL TITRATION RUN
EFFECT OF INITIATOR (AIBN) CONCENTRATION ON THE
THERMAL STABILITY OF PVC POLYMERISED at 60°C to ABOUT 60% CONVERSION

—○—○— 1.0 M%
—□—□— 0.1 M%
—△—△— 0.01 M%

initiation of the dehydrochlorination reaction especially if one would adopt the zipper reaction theory. This is followed by the fast unzipping of HCl through the backbone of the polymer chain accompanied by chain scission. The third phase R^2 could be liberating less HCl due to the fact that the unstable chlorine concentration in the polymer has been lowered by the first rate R^1, (any excess HCl due to branching and other weak sites due to chain imperfections have been eliminated) and the remaining polymer chains which now should have a high double bond population are either recombining to form longer chains or some of them are going through a process of cyclisation. The last phase will normally be accompanied with an increase in viscosity which would also explain the crosslinking reactions that follow.

2 - The second explanation is based on the physical factors which occur during the initial stages of degradation :

The inhibition period could be attributed to three physical phenomena :

a) Time required for HCl to reach saturation level

b) Time required for the volume displacement of the system (found to be about 2 minutes)

c) Increased mobility of the polymer as the clusters of polymer gels are dispersed and the lattice disentangled liberating trapped HCl.

This is followed by two different dehydrochlorination rates influenced by viscosity effects. Figure 4-26 shows the progress of the dehydrochlorination reaction and the changes in viscosity that occur simultaneously. It is seen how the viscosity drops to its minima after about half an hour coinciding with the end of the inhibition period. This leads us to phase two or R^1 where the HCl frozen by the previously mentioned physical obstacles is now freed and one notices the dehydrochlorination reaction competing with that of crosslinking. Hence after a very fast rate of dehydrochlorination and

a gentle slope in viscosity rise, the dehydrochlorination slows down as a sudden sharp increase in viscosity occurs after about 4 hours which will have the effect of slowing down the diffusion and escape of HCl which leads us to phase 3 or R^2.

In this last phase, the viscosity rate levels off accompanied by a slower rate of dehydrochlorination which could be due to the riddance of the main abnormal reactive group and the viscosity change. At the end of this phase there is an indication of yet another rate acceleration in the dehydrochlorination reaction.

Figure 4-3 shows how the inhibition period increases as the stability of the polymer (as we shall discuss later) increases, therefore, it should be considered in the studying of the overall rates of dehydrochlorination. Figures 4-4 and 4-5 show how the first fast rate (R^1) and the second slower rate (R^2) follow the same pattern with polymerisation temperature and percent conversion as the overall average rate (R), as shown in Figure 4-7.

The only difference being that R^1 shows a more prominant minima with a greater indication of decreasing stability with increase in polymer conversion.

Thus it was decided to use the average total rate of dehydrochlorination in this study based on :

1 - We could not substantiate a chemical explanation for the two different rates and hence be able to analyse each rate on its own merit.

2 - If it is due to a physical phenomena, it is difficult to determine the exact overlap or lag time of each phase.

3 - There is evidence that for polymers prepared at both high (above 100°) and low (below $0^{\circ}C$) temperatures, there is only one rate.

4 - All individual rates show the same trend and the different rates R^1 and R^2 add up to the accumulative total average rate R.

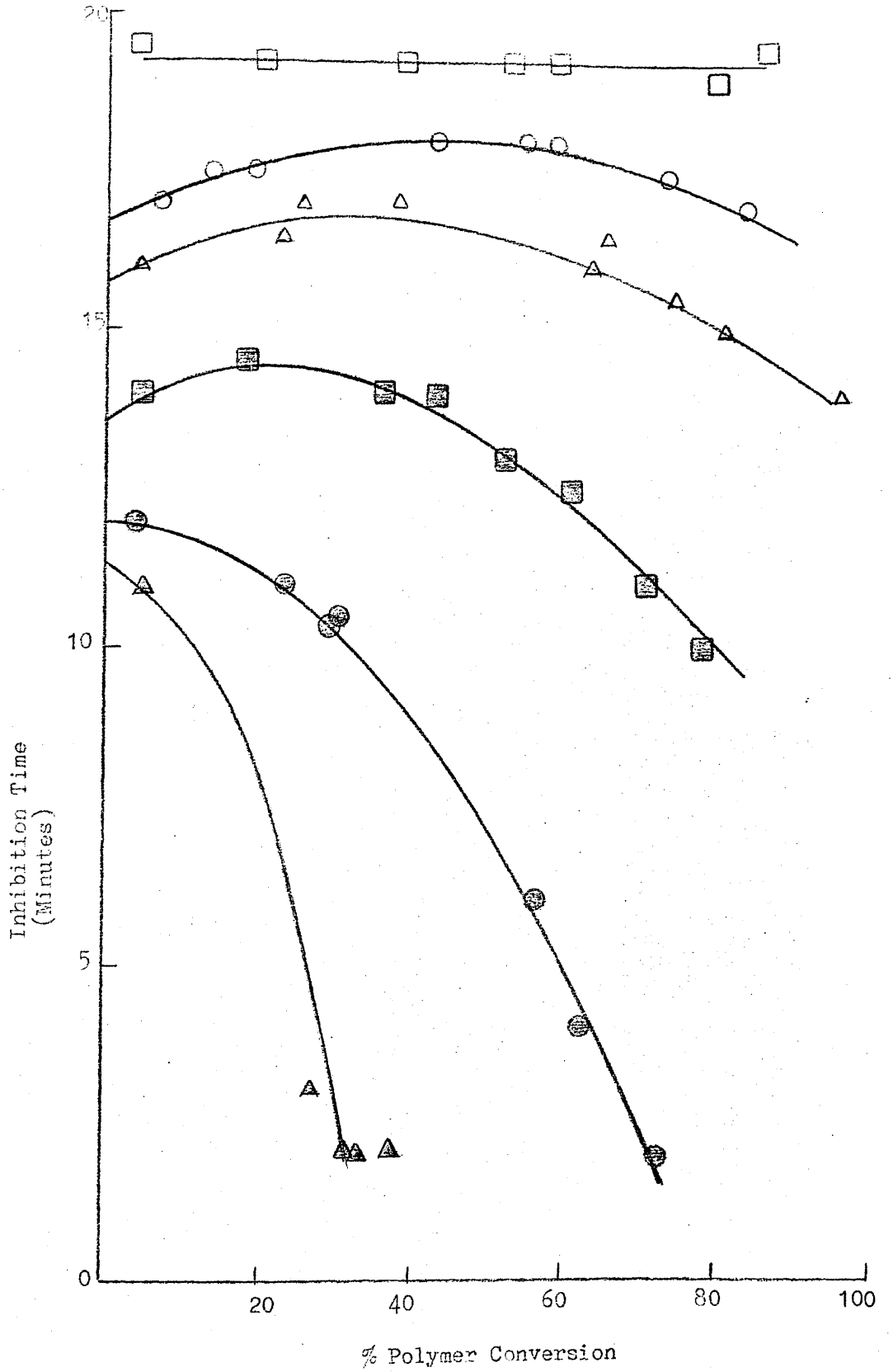


Fig. 4-3 EFFECT OF POLYMERISATION TEMPERATURE AND % POLYMER CONVERSION ON THE INHIBITION PERIOD OF THE DEHYDROCHLORINATION OF PVC INITIATED WITH Bz_2O_2 (From Top to Bottom 25°C - 40°C - 80°C - 100°C 120°C)

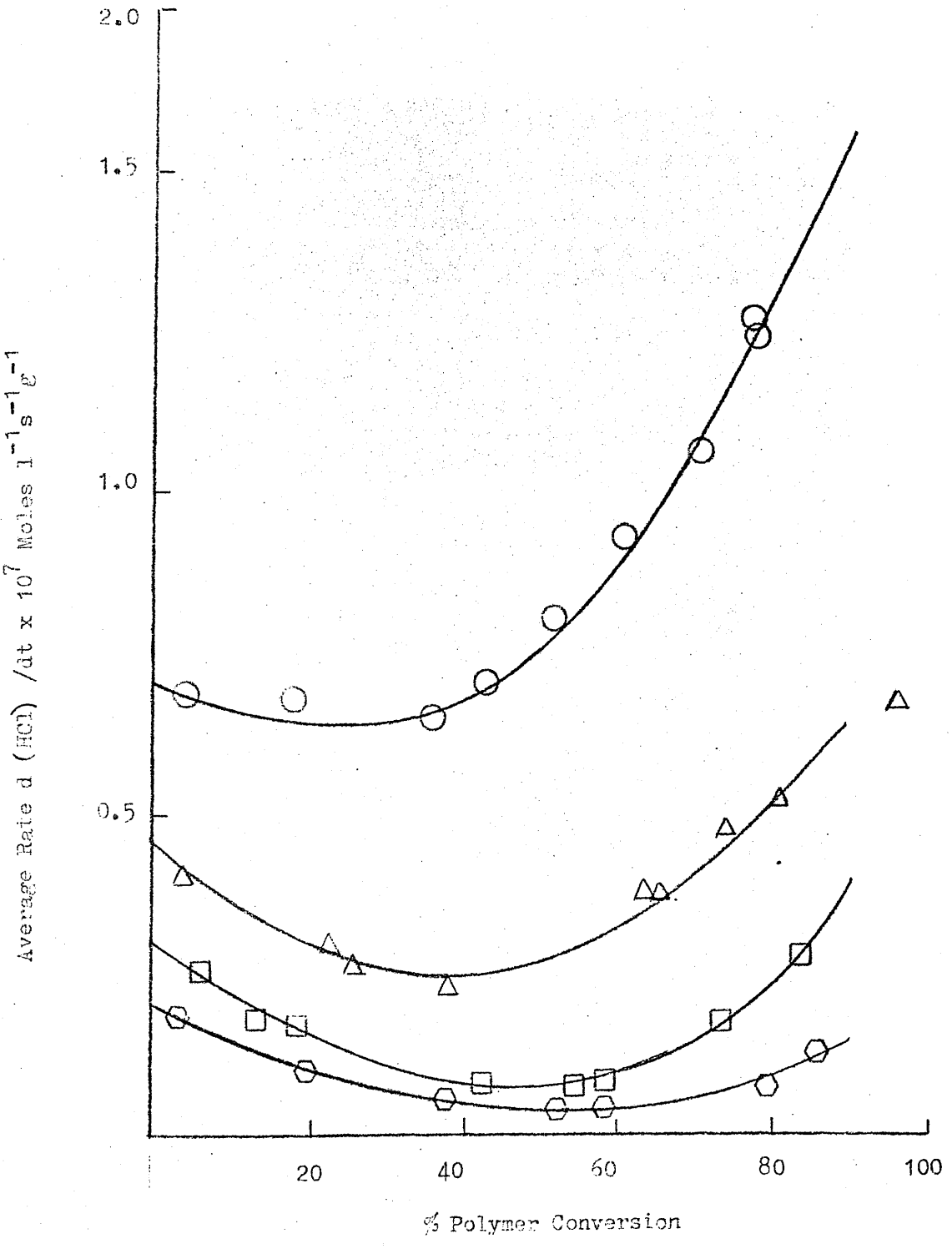


Fig. 4-4 FIRST RATE R^1 EFFECT OF POLYMERISATION TEMPERATURE ON RATE OF DEHYDROCHLORINATION (From top to bottom, 80°C, 60°C, 40°C, 25°C)

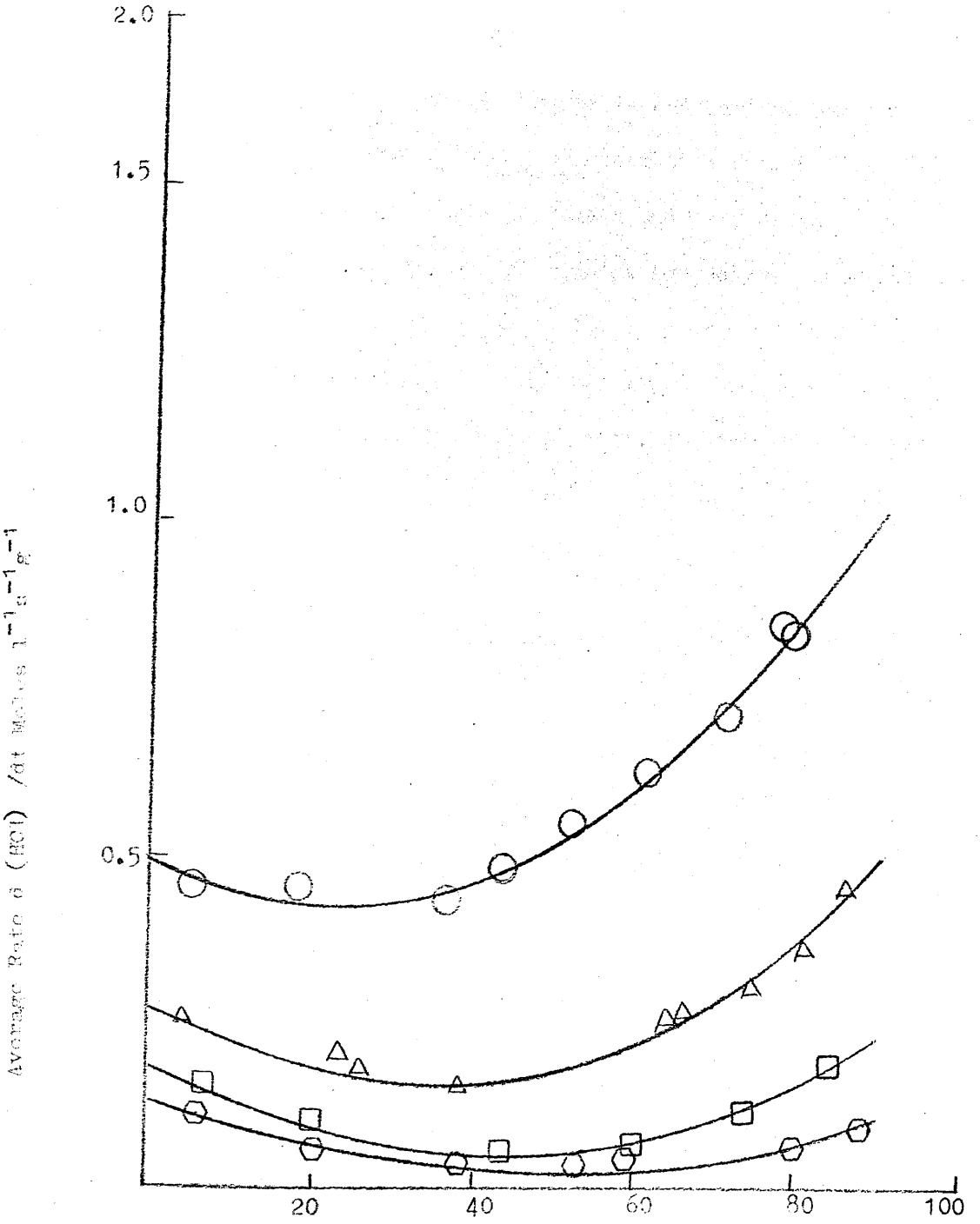


Fig. 4-5 EFFECT OF POLYMERISATION TEMPERATURE ON RATE OF DEHYDROCHLORINATION (R^2) (From top to bottom 80°C, 60°C, 40°C, 25°C)

Effect of Initiator Type and Concentration on the Thermal Stability of PVC

The rates of dehydrochlorination for PVC polymerised at 60°C using 0.01, 0.10 and 1.0 Mole % of Bz_2O_2 and AIBN are reported for different % polymer conversions in Table 4-1, (around 5% conversion) Table 4-2 (around 40% conversion) and table 4-3 (around 90% conversion).

An increase of Bz_2O_2 concentration from 0.01 to 1.0 M%, a one hundred fold increase, increases the rate of dehydrochlorination or instability of PVC by only 30% at low polymer conversions. This instability is magnified at 40% polymer conversion to a three fold increase and another large increase in the case of high polymer conversion where the rate of dehydrochlorination is increased by almost 3.5 fold when the initiator concentration is increased from 0.01 to 1.0 M%.

Table 4-1. Effect of Initiator Type and Concentration on the Thermal Stability of PVC Prepared at 60°C for low polymer % conversion

Initiator and Concentration M %	Polymer % Conversion	Total Average Rate $d[HCl]/dt \times 10^7$ Moles l^{-1} s^{-1} g^{-1}	Ratio of $d[HCl]/dt$ to Lowest Rate	Inhibition Time (Mins)	Ratio of Inhibition Time to Lowest Period
Bz_2O_2 :					
0.01	4.3	0.66	1.0	16.0	1.1
0.10	7.0	0.70	1.06	14.5	1.0
1.0	4.8	0.87	1.32	14.5	1.0
AIBN :					
0.01	4.0	0.62	1.0	16.0	1.03
0.10	4.3	1.03	1.66	15.5	1.0
1.0	5.3	1.23	1.98	15.5	1.0

Table 4-2. Effect of Initiator Type and Concentration on the Thermal Stability of PVC prepared at 60°C for medium polymer % Conversion

Initiator and Concentration M %	Polymer % Conversion	Total Average Rate $d[HCl]/dt \times 10^7$ Moles $l^{-1}s^{-1}g^{-1}$	Ratio of $d[HCl]/dt$ to Lowest Rate	Inhibition Time (Mins)	Ratio of Inhibition Time to Lowest Period
Bz_2O_2 :					
0.01	37.8	0.38	1.0	17.0	1.31
0.10	41.8	0.61	1.61	15.5	1.19
1.0	42.0	1.14	3.0	13.0	1.0
AIBN :					
0.01	44.9	0.28	1.0	17.5	1.25
0.10	37.0	0.79	2.82	16.5	1.18
1.0	41.9	1.57	5.61	14.0	1.0

Table 4-3. Effect of Initiator Type and Concentration on the Thermal Stability of PVC prepared at 60°C for high polymer % conversion

Initiator and Concentration M %	Polymer % Conversion	Total Average Rate $d[HCl]/dt \times 10^7$ Moles $l^{-1}s^{-1}g^{-1}$	Ratio of $d[HCl]/dt$ to Lowest Rate	Inhibition Time (Mins.)	Ratio of Inhibition Time to Lowest Period
Bz_2O_2 :					
0.01	96.0	1.14	1.0	14.0	1.33
0.10	90.0	1.41	1.24	12.5	1.19
1.0	94.2	1.58	3.39	10.5	1.0
AIBN :					
0.01	96.5	1.01	1.0	14.5	1.16
0.10	95.5	1.81	1.79	12.5	1.0
1.0	93.6	2.12	2.10	12.5	1.0

In case of AIBN, the effect of change of concentration on stability is more remarkable, where it increases by two fold at low conversions and about 5.5 fold for medium conversions but is only 2 fold greater for high conversions. With this last exception, it seems that the stability of PVC is more sensitive to changes in AIBN initiator concentration than to changes in Bz_2O_2 concentrations.

AIBN polymers are less stable than ones prepared with Bz_2O_2. At 1.0 M% concentration AIBN is less stable by about 40% for low and medium conversions and about 35% for high polymer conversions.

The same applies to the 0.10 M% initiator concentration but not to the same extent. However, at low initiator concentrations of 0.01 M% the trend is reversed and AIBN polymers are slightly more stable; about 5% for low conversions, 35% for medium and 13% for high conversions. Fig. 4-6 and shows the relation between the increase of initiator concentration and the decrease in stability of PVC for low; minima; and high conversions. Fig. 4-16 and 4-17 show how at 0.01 M% AIBN is more stable especially from medium to high conversion. At 0.1 M% Bz_2O_2 is more stable up to 70% and then becomes identical to AIBN and at 1.0 M% . There is a distinct increase of stability with Bz_2O_2 over AIBN. At 1.0 M% initiator concentration we obtain a straight slope with conversion and lo se the trough effect. The above results would indicate, that there is a direct relationship between increased initiator fragment concentration and increased instability. This relationship is affected by the rate of polymerisation at the different polymerisation reaction stages as indicated by the effect of polymer conversion. Bz_2O_2 polymers in general and at normal conversions are more stable than AIBN polymers. At low initiator concentration 0.01 the switch of improved stability to AIBN polymers could be due to a different decomposition mechanism of the Bz_2O_2 initiator giving less

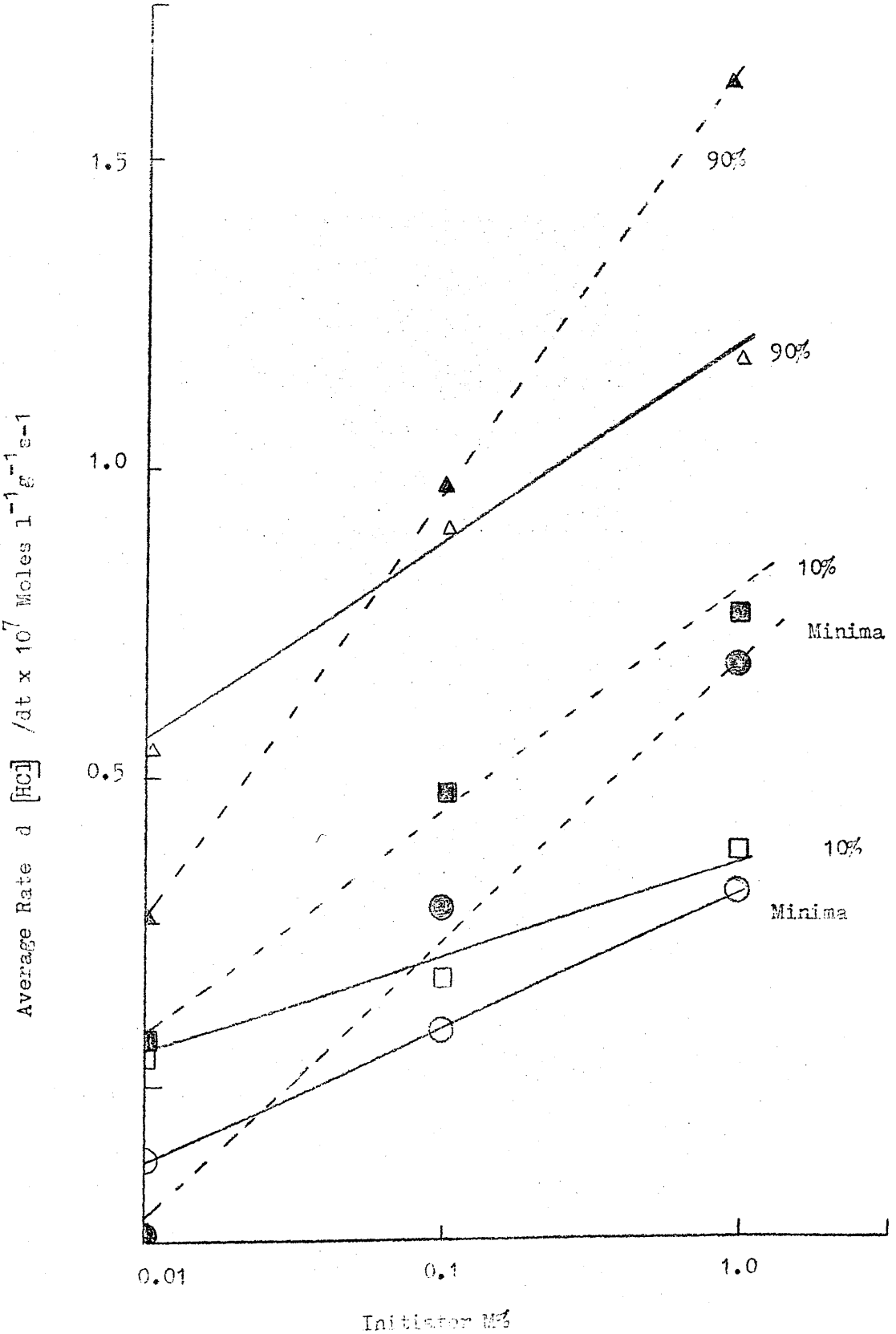
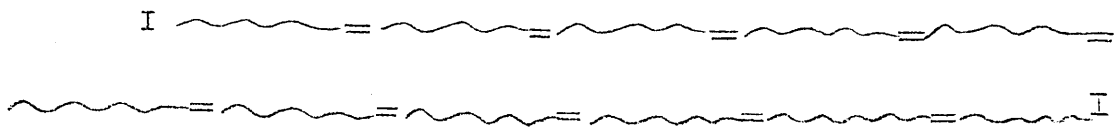


Fig. 4-6 EFFECT OF INITIATOR CONCENTRATION ON THE STABILITY OF PVC at 10%,'MINIMA' (minimum rate of dehydrochlorination) and 90% CONVERSION (Bz_2O_2 solid line AIBN broken line)

stable species at low polymerisation rates which could affect consequent chain transfer reactions or branching sites or the formation of double bonds. Another less rational explanation would be the existence of two different Bz_2O_2 initiator fragment species with one having a stabilising effect and the contribution of which is not noticed until a higher concentration is available. Also, although, the molecular weight of AIBN polymers are higher than those of Bz_2O_2 for all the three different initiator concentrations for low conversion polymers, the ratio is lowest for 0.01 M% concentration. (only 12% greater as opposed to about 40% difference in case of 1.0 M%).

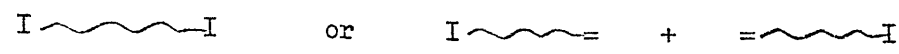
Increase in instability is relatively slight with increase in initiator end groups or at least not in proportion. A 100 fold increase in initiator concentration which increases the rate of initiation only by 1.5 or 2 fold, has the effect of increasing the rate of dehydrochlorination by only 5.5 fold in the extremist case. Also, the fact that at the initial stages of polymerisation the initiator fragments are more significant than for example at 40% conversion, yet we find much smaller changes in instability at low conversion than at 40%. This would indicate one of two things; either that at the early stage of initiation, initiators could in a competing reaction be contributing to the stability of the polymer or that initiator fragments by themselves do not have a negative effect on stability until they become involved in secondary reactions such as branching and transfer to polymer which would normally occur at later stages of polymerisation. Therefore as we improve the stability of PVC the initiator fragments contribution become more important.

Generally the more catalyst fragments the less stable the polymer is at low initiator concentration probably we have a situation of



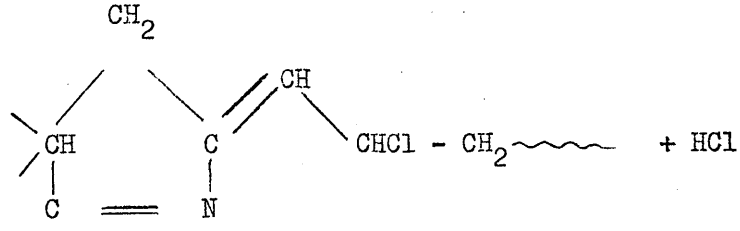
with about two initiator fragments per 11 or 12 polyene chains.

At high initiator concentration probably it is more like,



or a maximum of two initiator fragments per chain which will give a higher initiator fragment concentration per unit weight of polymer. This is also substantiated by the reported great drop of $\overline{DP}$ at high catalyst concentration.

The fact that AIBN polymers are less stable than those of Bz_2O_2 at higher AIBN concentration might be due to the possibility of cyclisation with vinyl chloride occurring to form :



A somewhat similar reaction has been reported for AIBN and acrylonitrile at relatively low temperatures.

The above is only a very tentitive explanation and not a very convincing one.

As we improve stability of PVC the initiator fragments contribution become more important.

Inhibition periods vary only slightly at low conversion for both initiators. At medium and high conversions inhibition tends to increase with decrease in initiator concentration.

In general AIBN polymers have a longer inhibition period regardless of conversion. The greatest increase in inhibition time is of the order of 30% and occurs with Bz_2O_2 polymer at both medium and high

conversion when initiator concentration is reduced from 1.0 to 0.01 M%.

In all cases the more stable the polymer (i.e. the lower the rate of dehydrochlorination) the longer is the inhibition period.

Table 4-4. Effect of Polymerisation Temperature on the Thermal Stability of PVC using 0.01 M% Bz_2O_2 initiator

Polymeris. Temp. °C.	Polymer % Conversion	Total Average Rate $d[HCl]/dt \times 10^7$ Moles $l^{-1}s^{-1}g^{-1}$	Ratio of $d[HCl]/dt$ to Lowest Rate	Inhibition Time Mins.	Ratio of Inhibition Time to Lowest Period
High Conversions :					
25	86.5	0.21	1.0	19.5	2.0
40	84.0	0.47	2.24	17.0	1.7
60	80.8	0.88	4.19	15.0	1.5
80	78.0	2.08	9.90	10.0	1.0
Medium Conversions :					
25	38.5	0.10	1.0	19.25	1.38
40	43.0	0.13	1.30	18.0	1.29
60	37.8	0.38	3.80	17.0	1.21
80	43.0	1.19	11.90	14.0	1.0
Low Conversions :					
25	4.2	0.30	1.0	19.5	1.39
40	6.7	0.42	1.40	17.0	1.21
60	4.3	0.66	2.20	16.0	1.14
80	4.7	1.14	3.80	14.0	1.0

Effect of Polymerisation Temperature on The Thermal Stability of PVC.

Table 4-4 shows the rates of dehydrochlorination for Bz_2O_2 initiated PVC over a 55°C polymerisation temperature range. From these results it is evident that the thermal stability of PVC decreases as the polymerisation temperature increases.

The 80°C polymer at high conversion is the least stable whereas at 25°C it is the low conversion polymer that is least stable.

The effect of increase in temperature is most evident in the medium conversions of about 40% where the rate of dehydrochlorination is increased by almost 12 fold from 25°C to 80°C polymers. This effect decreases slightly with high conversion polymers where a 10 fold increase occurs while the minimum change occurs with low conversion where only a four fold increase manifests itself over the same temperature range.

The medium conversions are the most stable over the complete polymerisation temperature range except at 80°C. The most stable is PVC polymerised at 25°C to about 40% conversion as opposed to the least stable polymer obtained at 80°C and about 80% conversion. The rates are 1.10×10^{-7} and 2.08×10^{-7} Moles $l^{-1}s^{-1}g^{-1}$ or an increased instability of about 20 fold.

The results of Table 4-4 are shown in Fig. 4-7. Each temperature curve manifests a minima in terms of rate of dehydrochlorination in relation to % polymer conversion indicating maximum stability at medium polymer conversions and increased instability at both ends of the conversion scale. This minima shifts to a lower conversion 52,46,38, 20% as the polymerisation temperature increases from 25, 40, 60, 80°C respectively. With this shift in minima there is also a steepening of the slope for high conversions, indicating that the rate of instability increases much faster for high conversion polymers as the polymerisation

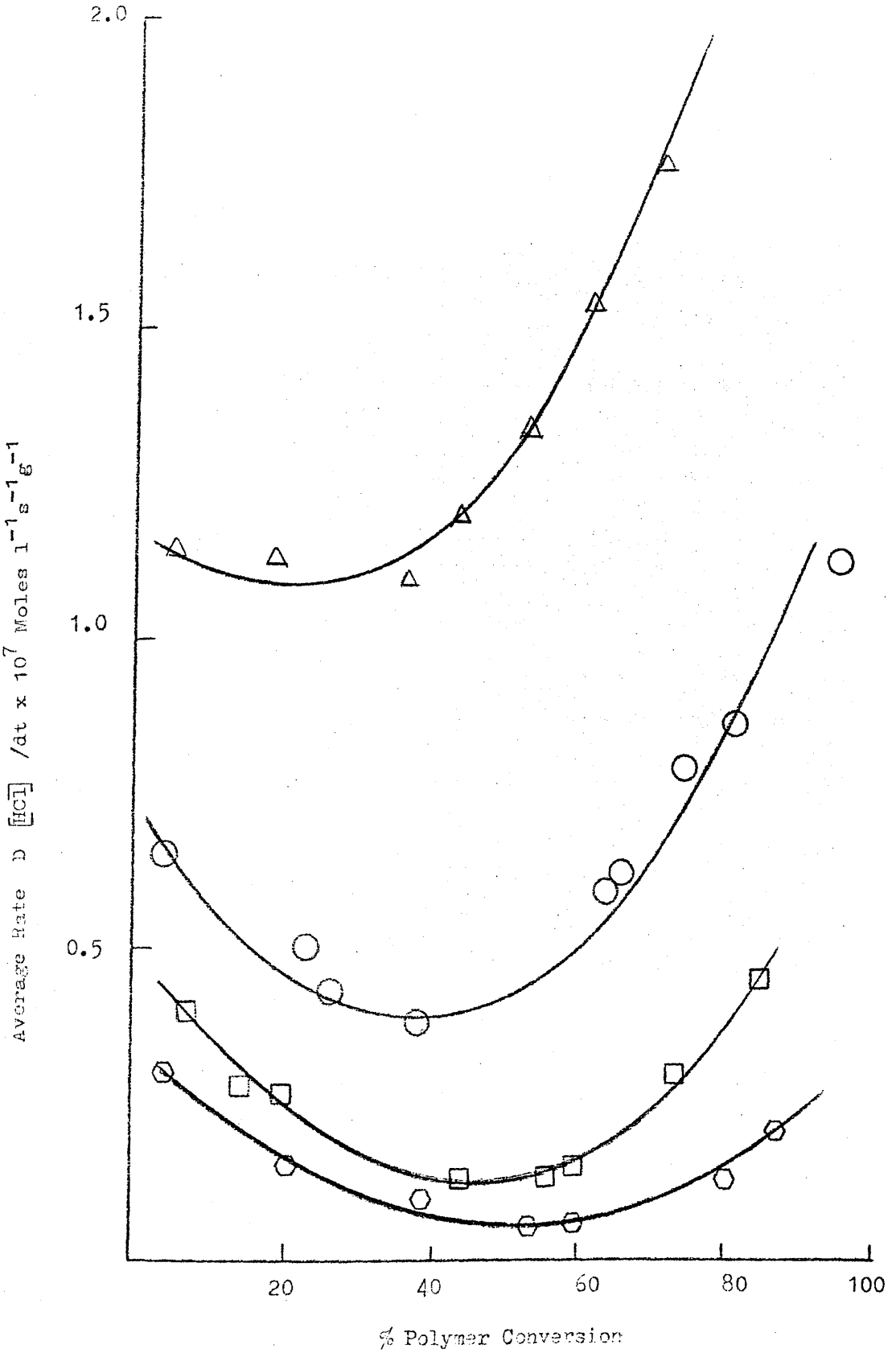


Fig. 4-7 EFFECT OF POLYMERISATION TEMPERATURE ON THE THERMAL STABILITY OF PVC POLYMERISED WITH 0.01 M% Bz_2O_2 FOR DIFFERENT % CONVERSIONS. TOTAL AVERAGE RATE (from top to bottom 25°C, 40°C, 60°C, 80°C)

temperature increases. This is in contrast to low conversion material where the effect of increase in temperature is not as marked.

One would expect more chain transfer to polymer in medium and high conversions which in turn is affected more by high temperature than by low temperatures. At low conversion the temperature effect influences mainly the chain transfer to monomer reaction and double bond formation.

Temperature dependence is slightly greater for higher initiator concentration of 0.1 M% as seen in Table 4-5, however, the pattern is identical.

Table 4-5. Effect of Polymerisation Temperature on the Thermal Stability of PVC using 0.1 M% Bz_2O_2 Initiator

Polymerisation Temperature °C.	Polymer % Conversion	Total Average Rate $d[HCl]/dt \times 10^7$ Moles $l^{-1}s^{-1}g^{-1}$	Ratio of $d[HCl]/dt$ to Lowest Rate	Inhibition Time Mins.	Ratio of Inhibition Time to Lowest Period
High Conversions :					
60	82.0	1.17	1.0	13.5	1.69
80	81.5	3.01	2.57	8.0	1.0
Medium Conversions :					
60	41.8	0.61	1.0	15.5	1.24
80	39.0	1.53	2.51	12.5	1.0
Low Conversions :					
60	7.0	0.70	1.0	14.5	1.04
80	6.0	1.42	2.0	14.0	1.0

Table 4-6 shows the results obtained for AIBN using the same initiator concentration of 0.01 M%.

The same pattern as in Bz_2O_2 is observed, a general decrease in stability with increase in polymerisation temperature with conversion being a major influencing factor. Medium conversion being the most stable and high conversion being least stable. The extent of change in stability for similar conversions over a temperature range of 40°C is slightly higher than in the case of Bz_2O_2. At medium conversion where the greatest change occurs, there is a 9.62 fold increase between 40° and 80°C polymers as opposed to 9.15 for Bz_2O_2.

These results are plotted in fig. 4-8

Table 4-6. Effect of Polymerisation Temperature on the Thermal Stability of PVC using 0.01 M% AIBN Initiator

Polymerisation Temperature °C.	Polymer % Conversion	Total Average Rate $d[HCl]/dt \times 10^7$ Moles $l^{-1}s^{-1}g^{-1}$	Ratio of $d[HCl]/dt$ to Lowest Rate	Inhibition Time (Mins.)	Ratio of Inhibition Time to Lowest Period
High Conversions :					
40	81.5	0.30	1.0	17.5	1.52
60	87.5	0.73	2.43	15.5	1.35
80	81.7	1.73	5.77	11.5	1.0
Medium Conversions :					
40	41.0	0.13	1.0	18.5	1.37
60	44.9	0.28	2.15	17.5	1.30
80	44.0	1.25	9.62	13.5	1.0
Low Conversions :					
40	6.2	0.35	1.0	18.0	1.33
60	4.0	0.63	2.10	16.0	1.19
80	4.3	1.22	3.49	13.5	1.0

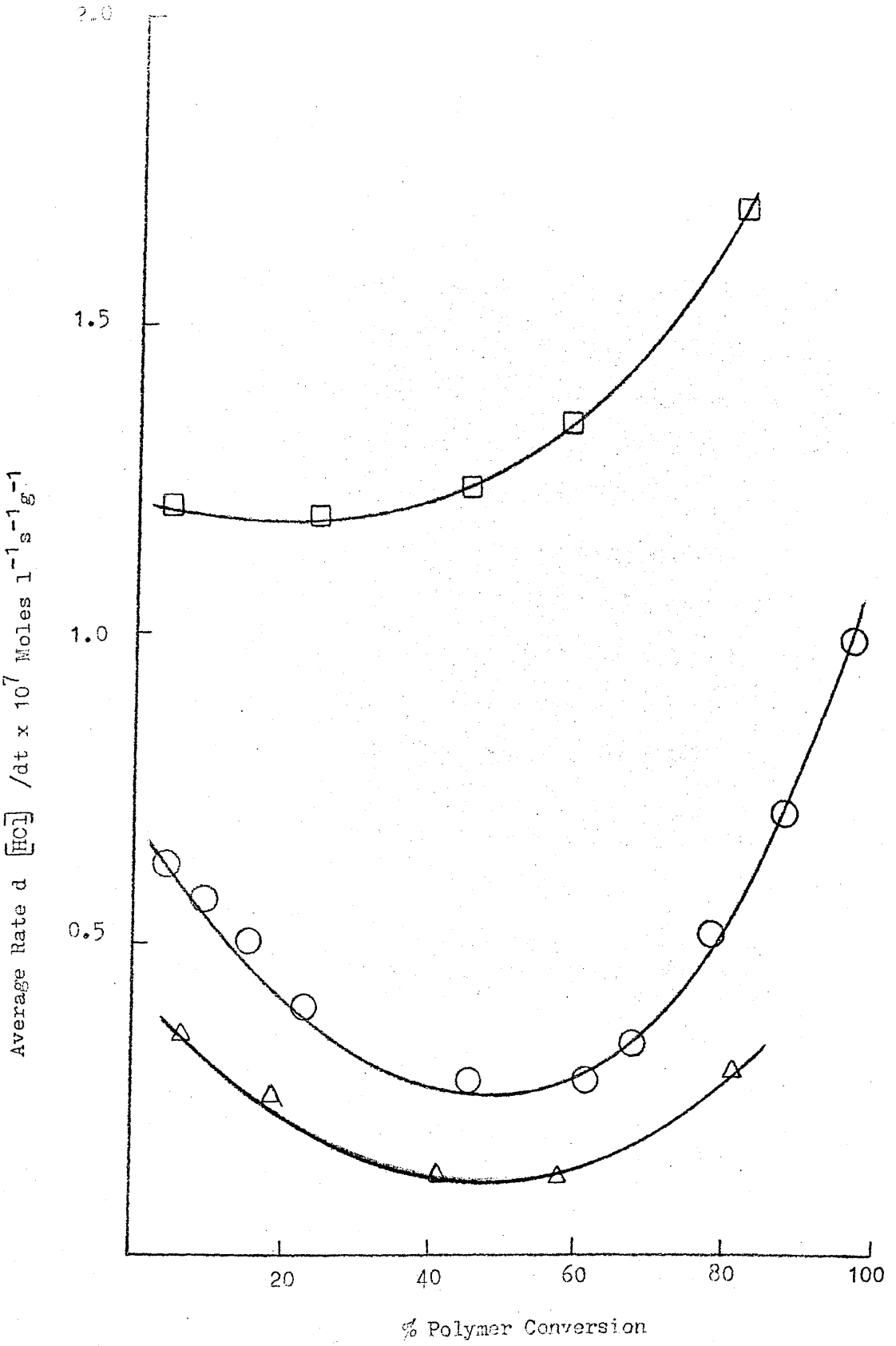


Fig. 4-8 EFFECT OF POLYMERISATION TEMPERATURES ON THE THERMAL STABILITY OF PVC WITH 0.01 M% AIBN FOR DIFFERENT % CONVERSIONS. (From top to bottom 80°C, 60°C and 40°C).

AIBN initiated polymers at 40°C have the same stability as Bz_2O_2 polymers at medium conversions but are less stable at both low and high conversions. With rise of polymerisation temperature to 60°C AIBN polymers become less stable over the whole conversion range but less so at the low end. AIBN polymers made at 80°C are more stable at low conversions up to 50% conversion. The general trend being that at higher conversions AIBN initiated polymers are less stable than those initiated with Bz_2O_2. Figure 4-9 shows the relationship of both AIBN and Bz_2O_2 initiated polymers as affected by temperature at one conversion (60%). Only slight differences in inhibition periods accompanied by major changes in rates with increase in temperature are observed.

In Figure 4-10 and Figure 4-11 the logarithm of d [HCl] /dt is plotted against the reciprocal of the absolute temperature of polymerisation, for both Bz_2O_2 and AIBN polymers, respectively in order to obtain the temperature coefficients shown in Table 4-7.

Table 4-7. Temperature coefficients for 0.01 M% Bz_2O_2 and AIBN polymers for different conversions

Initiator	% Polymer Conversion	Temperature Coefficient (k cal $Mole^{-1}$)	Ratio of (E) to smallest value
Bz_2O_2	5	5.2	1
	Medium Conversion corresponding to 'minima' in d [HCl] /dt	11.5	2.2
	90	8.0	1.6
AIBN	5	6.6	1
	Medium ccorresponding to 'minima' in d [HCl]/dt	12.6	1.9
	90	8.6	1.3

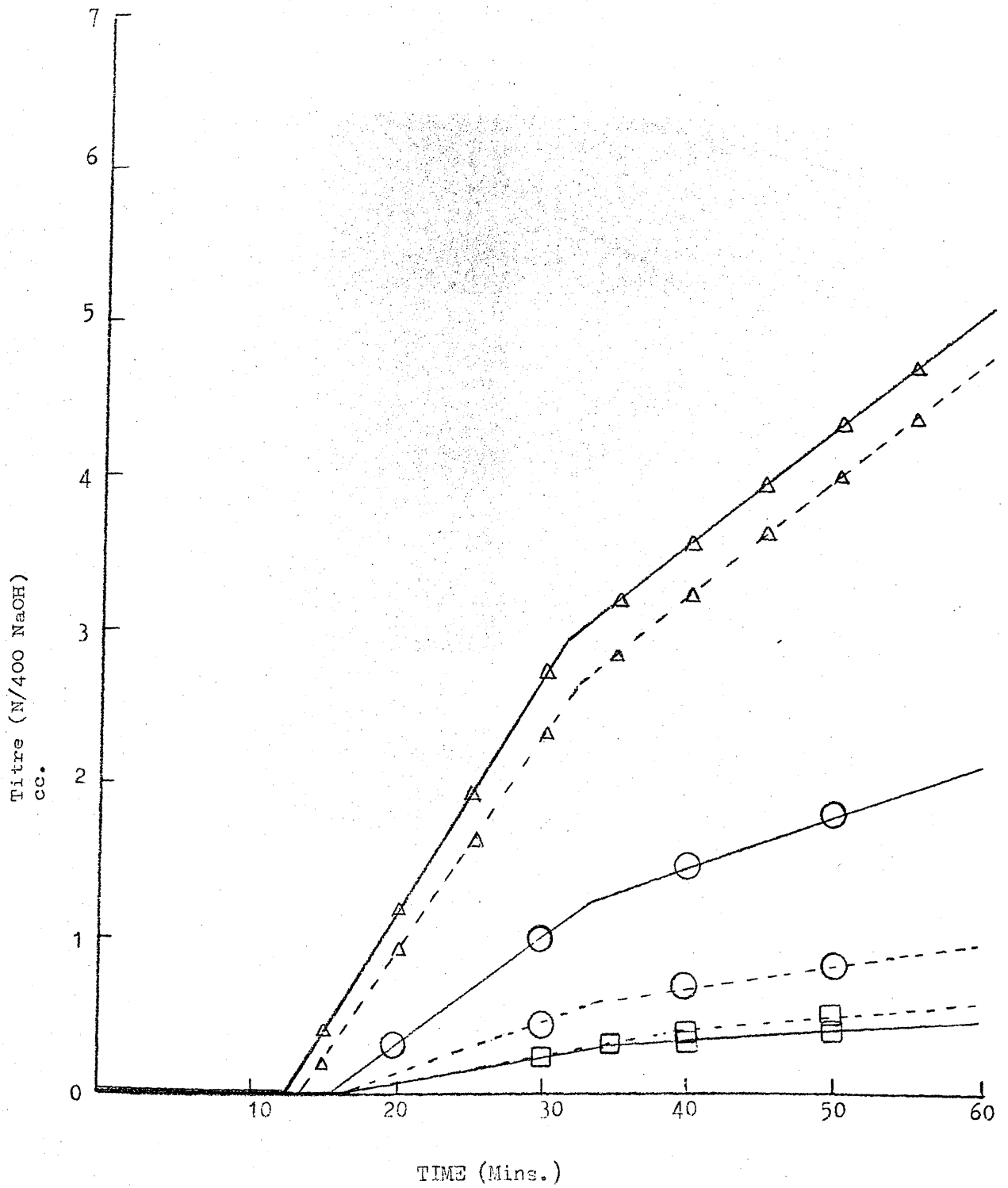


Fig. 4-9 REPRODUCTION OF TYPICAL TITRATION RUNS. EFFECT OF INITIATOR TYPE ON THERMAL STABILITY OF PVC PREPARED AT 40°C—□—□—, 60°C—○—○— and 80°C—△—△— USING 0.01 M% Bz_2O_2 (solid line and AIBN (Broken line) to about 60% CONVERSION.

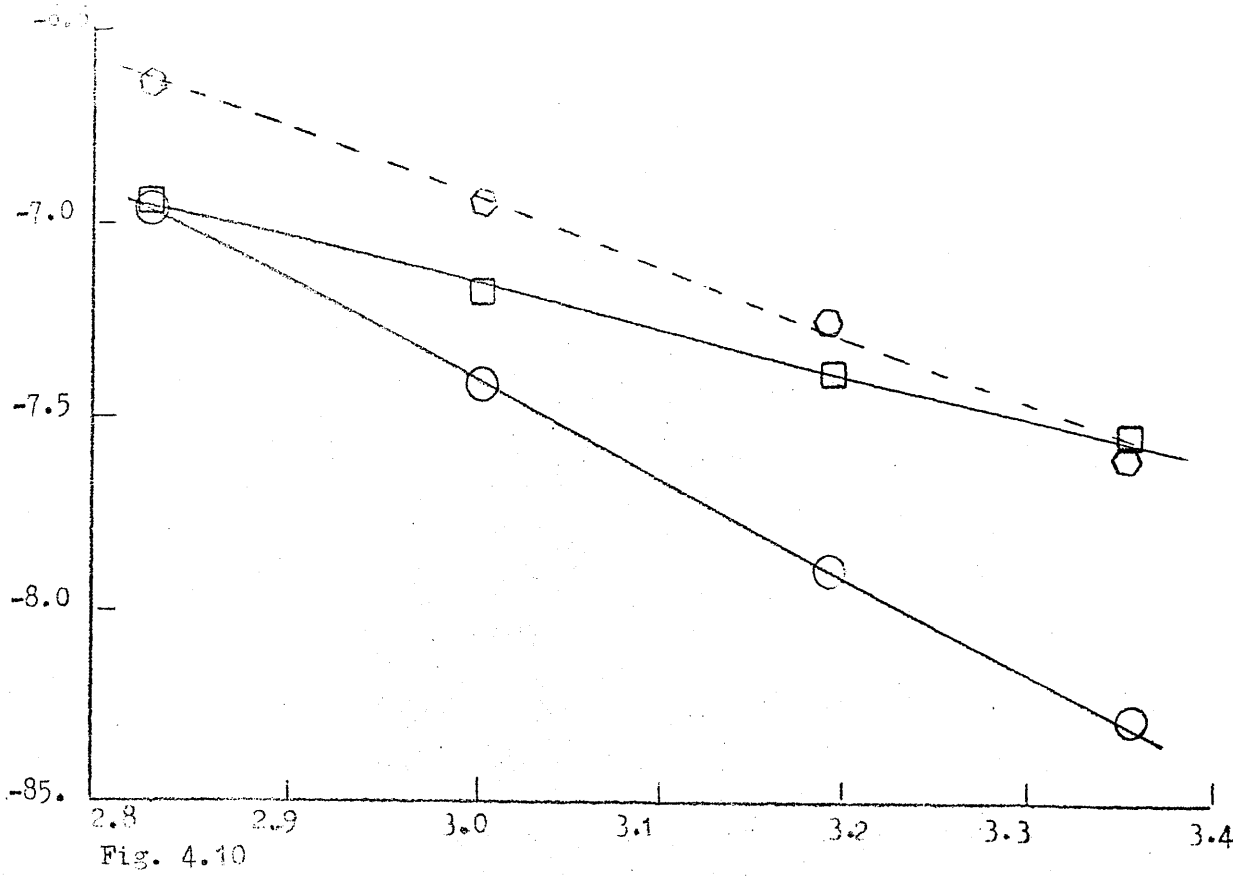


Fig. 4.10

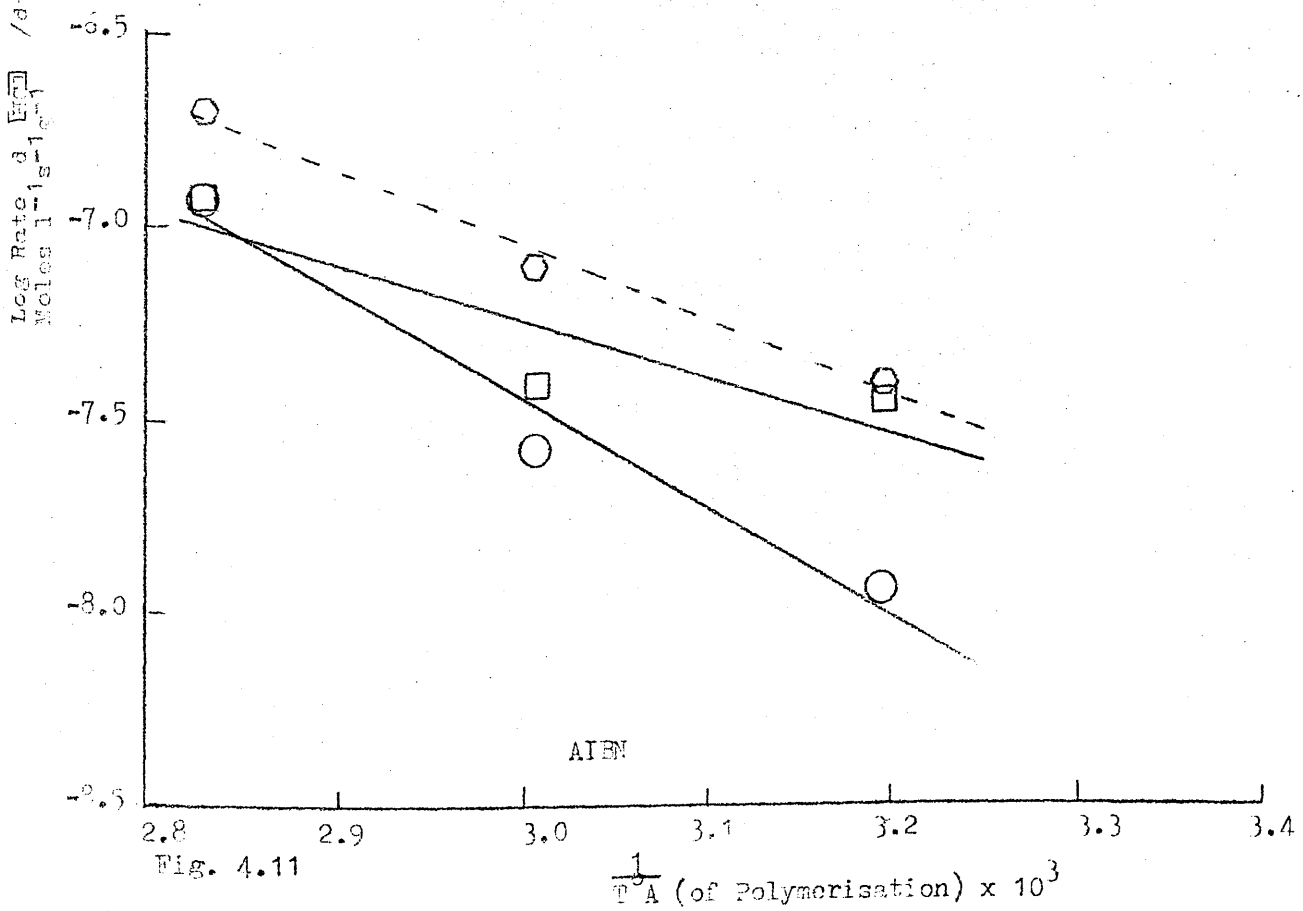


Fig. 4.11

Fig. 4-10 TEMPERATURE COEFFICIENT FOR Bz_2O_2 INITIATED PVC

Fig. 4-11 TEMPERATURE COEFFICIENT FOR AIBN INITIATED PVC

—□—□— Low Conversion ≈ 5% —○—○— Mod. Conversion Slopes of d [M] /dt

—○—○— High Conversion ≈ 20%

With Bz_2O_2 there is a good fit for a straight line relation with all three conversions. AIBN best line fit is the one for high conversion followed by the medium 'minima' conversion. Table 4-7 shows that the highest values in both cases were obtained at the medium conversions 11.5 and 12.6 k cal mol^{-1} and the lowest for low conversions 5.2 and 6.6 k cal $mole^{-1}$. AIBN shows slightly higher values than Bz_2O_2 at all three conversions and both follow the ratio of about 1 : 1.5 : 2 (Low : High : Medium conversions) or (E) Low Conversion = 0.5 (E) Medium Conversion and (E) High Conversion = 0.67 (E) Medium Conversion.

High temperature polymerisation was also investigated over the range of 80°C to 140°C. The reliability at these high temperatures especially due to the onset of a competitive degradation reaction during polymerisation (except for 80°C) cannot be assured as indicated by discolouration. Table 4-8 shows some of the results obtained. The most unstable polymer at 140°C gives a dehydrochlorination rate of 12.67 c 10^{-7} which is 8 fold larger than that 80°C and 125 fold greater than Bz_2O_2 initiated PVC at 25°C.

Table 4-8. Effect of high temperature of polymerisation on the thermal stability of PVC using 0.1 M% Bz_2O_2

Polymerisation Temperature °C.	Polymer % Conversion	Total Average Rate $d[HCl]/dt \times 10^7$ Moles $l^{-1}s^{-1}g^{-1}$	Ratio of $d[HCl]/dt$ to lowest Rate	Inhibition Period (Mins.)	Ratio of Inhibition Time to Lowest Period
80	6.0	1.42	1.03	14.0	1.8
	19.5	1.38	1.0	13.5	1.7
	39.0	1.53	1.11	12.5	1.6
	63.0	2.15	1.56	10.3	1.3
	81.5	3.01	2.18	8.0	1
100	4.3	1.72	1.0	12.0	6.0
	28.3	2.11	1.23	10.5	5.25
	62.5	3.38	1.97	4.0	2.0
	72.5	4.75	2.76	2.0	1.0
120	5.0	1.94	1.0	11.0	5.5
	26.6	4.0	2.06	3.0	1.5
	37.2	6.57	3.39	2.0	1.0
140	3.0	2.08	1.0	10.5	5.3
	10.8	2.90	1.39	6.0	3.0
	18.0	4.75	2.28	2.0	1.0
	38.4	12.67	6.09	2.0	1.0

Inhibition periods dropped from 14 minutes for 80°C polymer to 2 minutes for 140°C polymer.

Actually the results are more encouraging, in their consistency, than anticipated. They indicate the continuation of the change in pattern in the rate/conversion/temperature curves as shown in figure 4-12. The

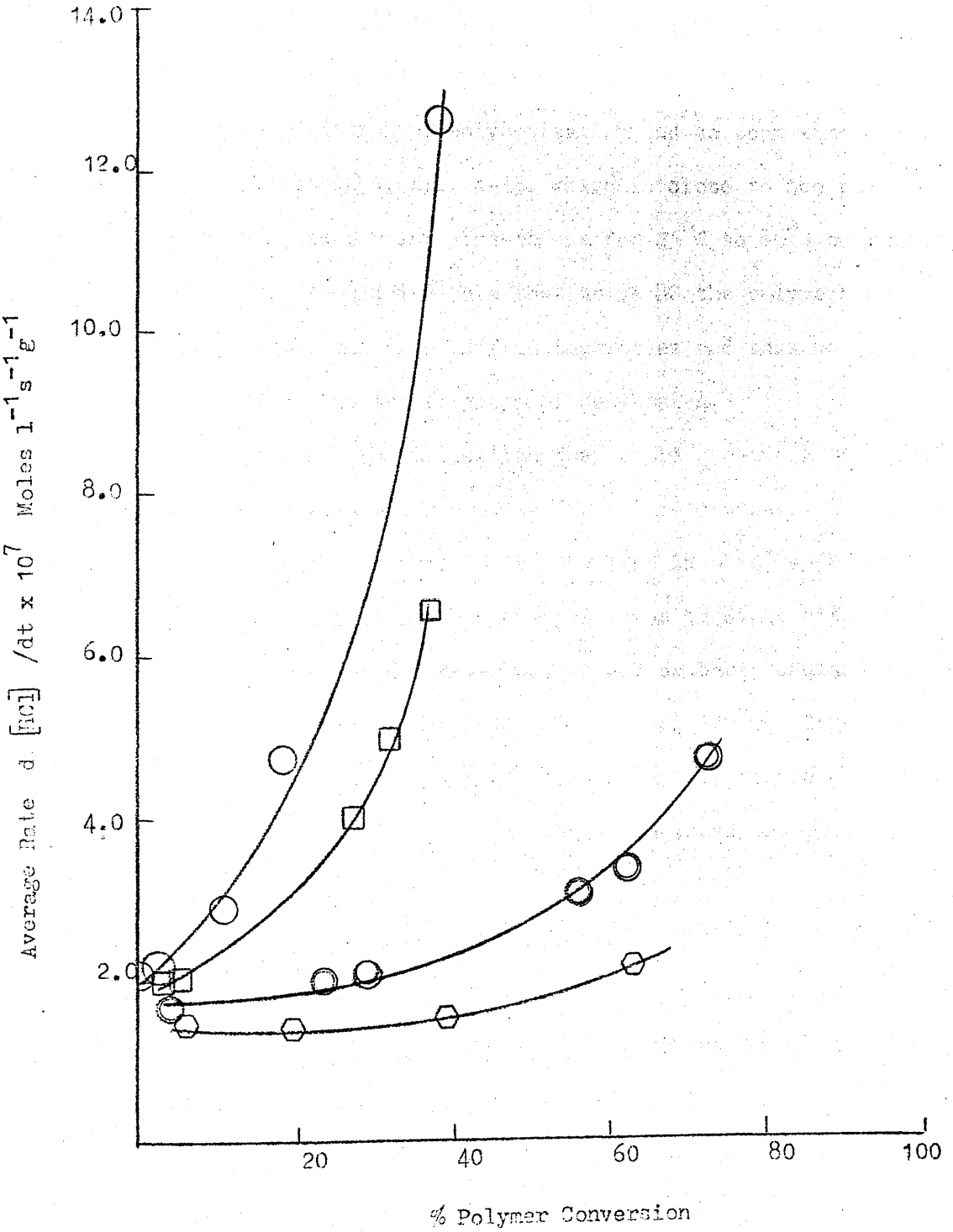


Fig. 4-12 EFFECT OF HIGH TEMPERATURE POLYMERISATIONS ON THE THERMAL STABILITY OF PVC POLYMERISED WITH 0.1 M% B_2O_2 FOR DIFFERENT % CONVERSIONS (From top to bottom 140°C, 120°C, 100°C and 80°C)

minima shifts to lower conversions with increase in temperature and is at zero conversion at 100°C. Plot of rate against conversion rising steeply with increase in conversion at temperatures above 100°C with a 6 fold increase of rate from 3% to 38% conversion for 140°C polymer. Log rate at 20% polymer conversion was plotted against the reciprocal absolute temperatures of polymerisation and an approximate (E) value of 5.96 was obtained, fig. 4-13, which is close to the previous figures obtained for low conversions for 25°C to 80°C polymerisations.

The above would indicate that above 80 the polymers are as unstable as polymer created from impurities and thus we do not get any stabilisation with the progress of conversion.

With proper identification they could provide a more factual model of an unstable PVC species for future studies. The temperature effect on initial conversion is much less in this temperature range, than the same effect at lower temperatures to start with the polymer obtained was low in molecular weight and probably contained a substantial double bond sequence especially the 120 and 140°C polymers which were slightly yellow. There was also a substantial increase in viscosity after degradation, up to 3 fold the undegraded viscosity in some cases.

Polymers prepared at the other end of the temperature scale were degraded in a similar fashion, the results are shown in Table 4-9. It is evident that polymers produced at these temperatures are high in molecular weight more crystalline and are much more stable. The effect of polymerisation temperature on crystallinity is shown in Fig. 4-14 as obtained from the ratio of the 635/690 cm^{-1} infra red absorbance peaks indicating maximum crystallinity at - 25°C. The effect of temperature is a continuous one down to about - 50°C where there is an indication of levelling off. The rates of hydrochlorination increase by 3 fold from - 75°C to 0° C and the inhibition period is, at a

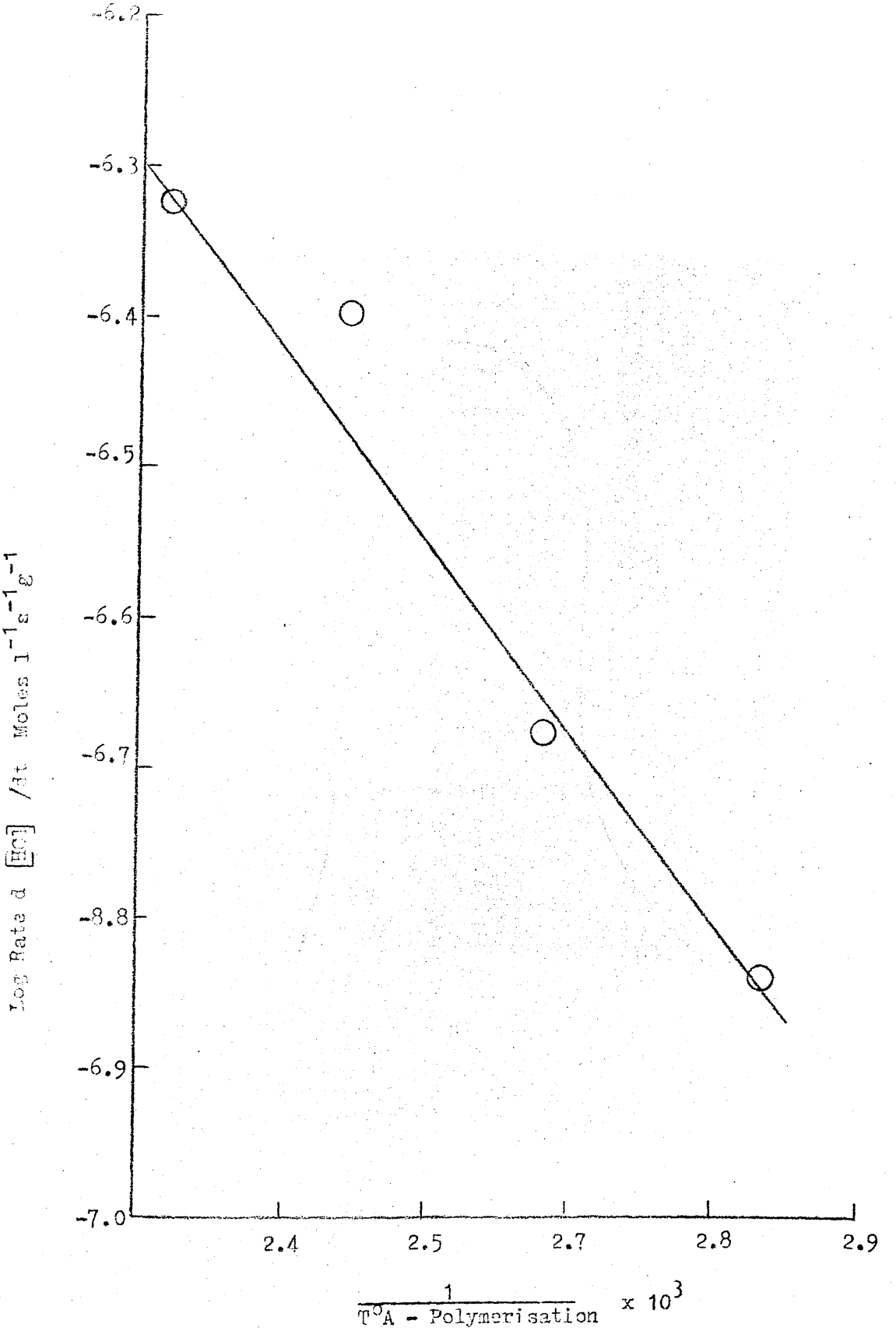


Fig. 4-13 TEMPERATURE COEFFICIENT PLOT OF TEMPERATURES OF POLYMERISATION ($80^{\circ}C$ to $140^{\circ}C$) AGAINST RATE OF DEHYDROCHLORINATION FOR 2% POLYMER CONVERSION

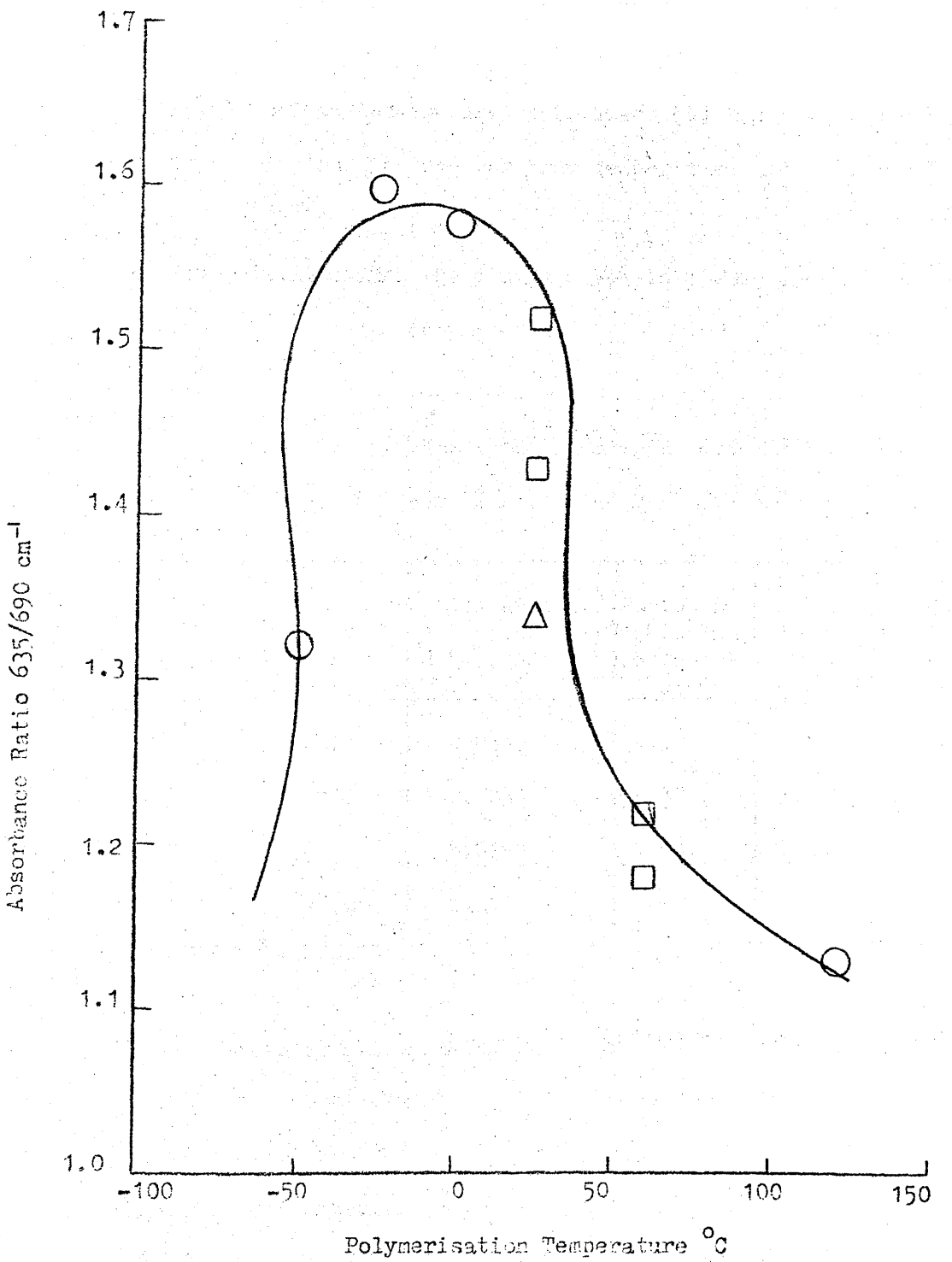


Fig. 4-14 EFFECT OF POLYMERISATION TEMPERATURE ON CRYSTALLINITY

□ Different Conversions
△ Photoinitiated Polymer

maxima at 0°C (32.5 mins.), and drops down to (20.5 mins) at - 75°C. There is also substantial chain scission indicating that low temperature polymerisation might produce links that are easily severed. Termination probably is more prevalent in these polymers than chain transfer.

The plot for the temperature coefficient (E) fig. 4-15, produced a much better fit than the one for high temperature and a value of 1.902 (k-cal mole^{-1}) for (E).

At lower temperatures the minima moves to higher conversions until a horizontal slope is obtained at 0°C.

Table 4-9. Effect of Low Temperature Photo-Polymerisations on the Thermal Stability of PVC using 0.01 M % AIBN.

Polymerisation Temperature °C.	Polymer % Conversion	Total Average Rate d [HCl]d/t Moles $l^{-1}s^{-1}g^{-1}$	Ratio of d[HCl]/dt to lowest Rate	Inhibition Time (Mins.)	Ratio of Inhibition Time to Lowest Period
0	20.3	0.033	3.30	32.5	1.6
- 25	22.2	0.023	2.30	26.0	1.3
- 50	19.6	0.015	1.50	24.5	1.2
- 75	18.0	0.010	1.0	20.5	1.0

Effect of Polymerisation Conversion on the Thermal Stability of PVC

The thermal stability of PVC produced at various extents of conversion to polymer for two different initiators at twelve different temperatures, was investigated.

The degradation were all carried out in solution at 198°C and the results for a typical conversion/dehydrochlorination rate relation is shown in table 4-10, for both Bz_2O_2 and AIBN. Fig. 4-16 and 4-17

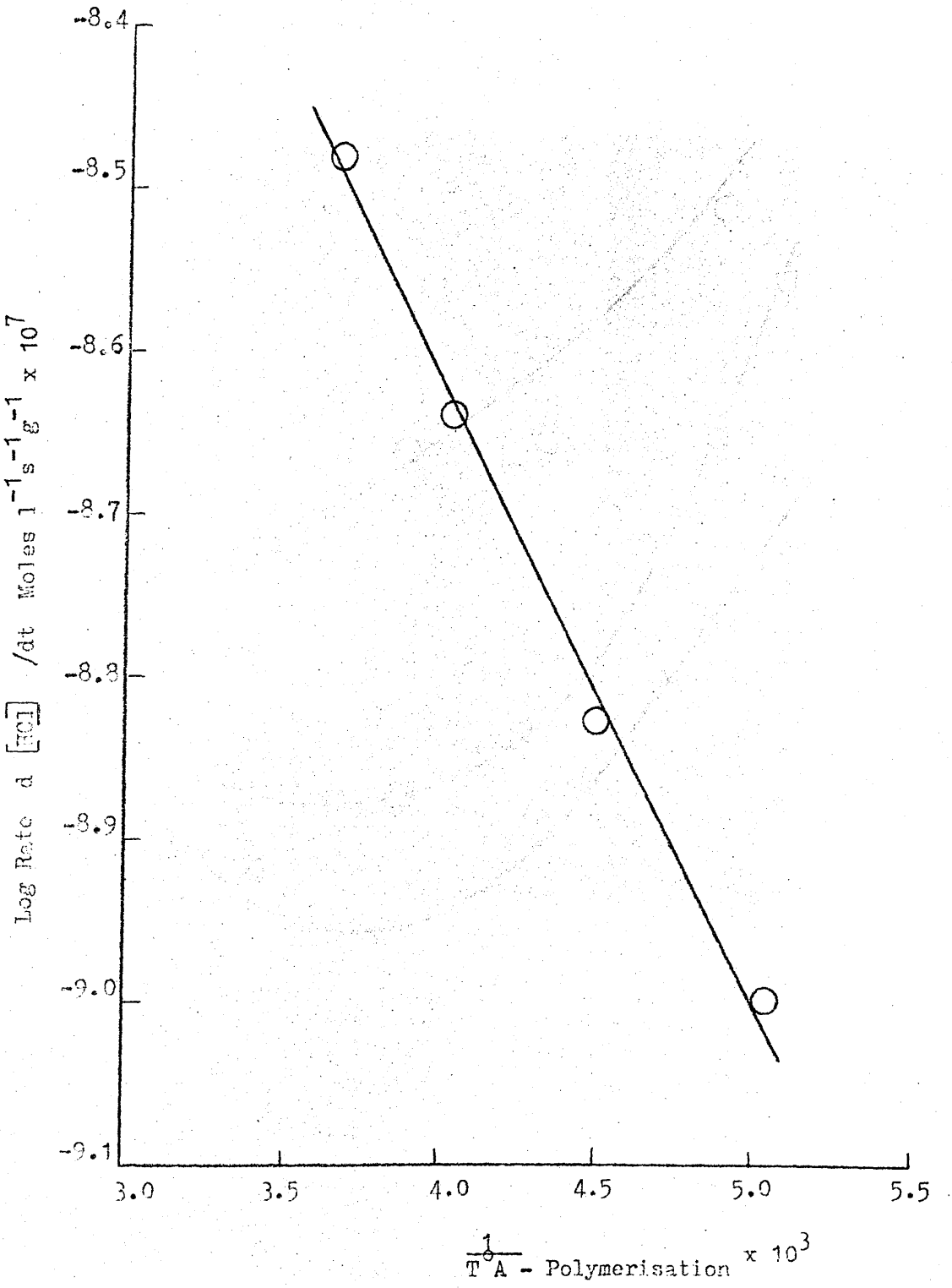


Fig. 4-15 TEMPERATURE COEFFICIENT PLOT OF TEMPERATURE OF SUB $0^{\circ}C$ POLYMERISATION AGAINST RATE OF DEHYDROCHLORINATION

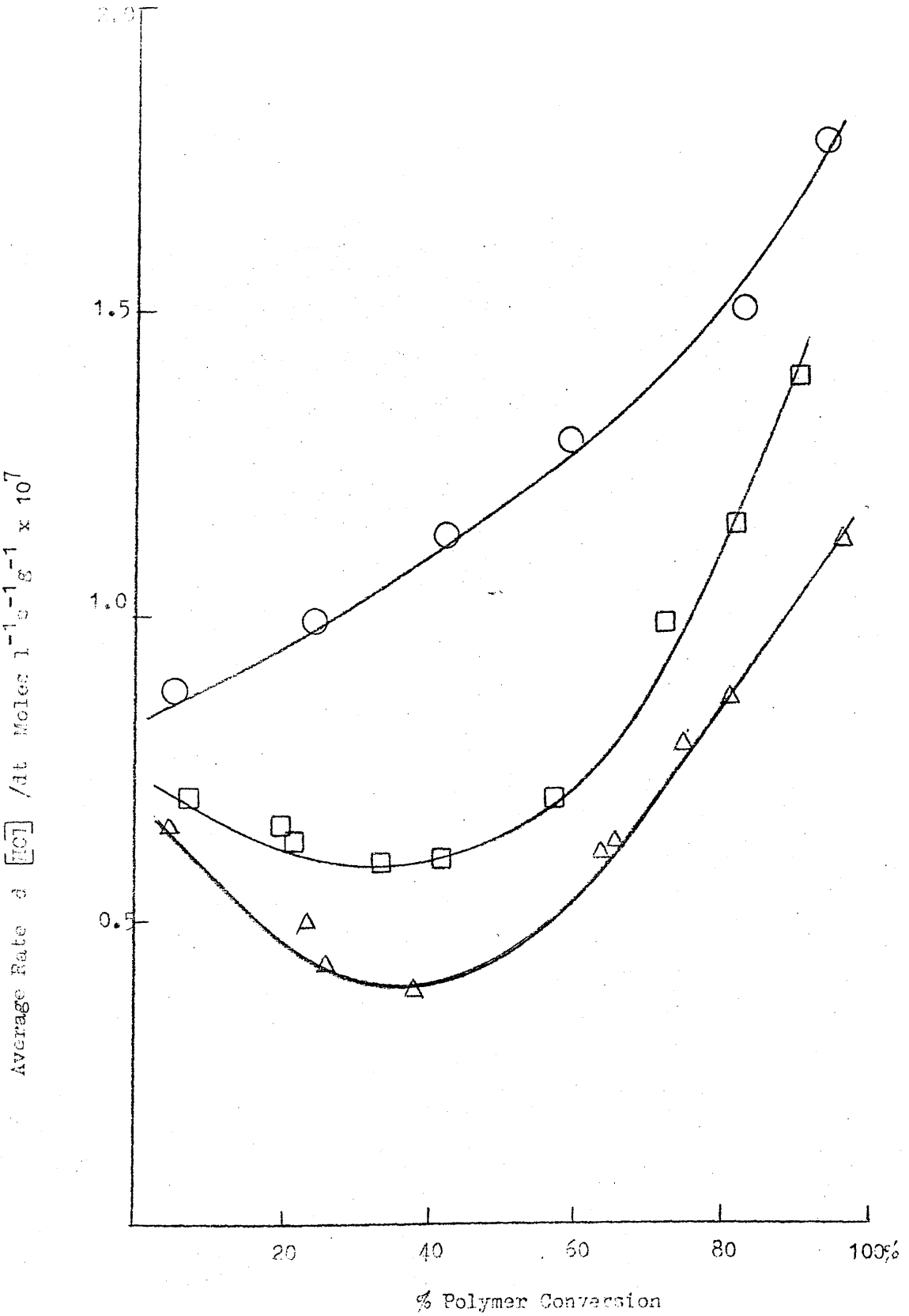


Fig. 4-16 EFFECT OF Bz_2O_2 INITIATOR CONCENTRATION ON THE THERMAL STABILITY OF PVC POLYMERISED AT 60°C FOR DIFFERENT % CONVERSIONS. (From top to bottom 1.0M%, 0.1 M% and 0.01 M%)

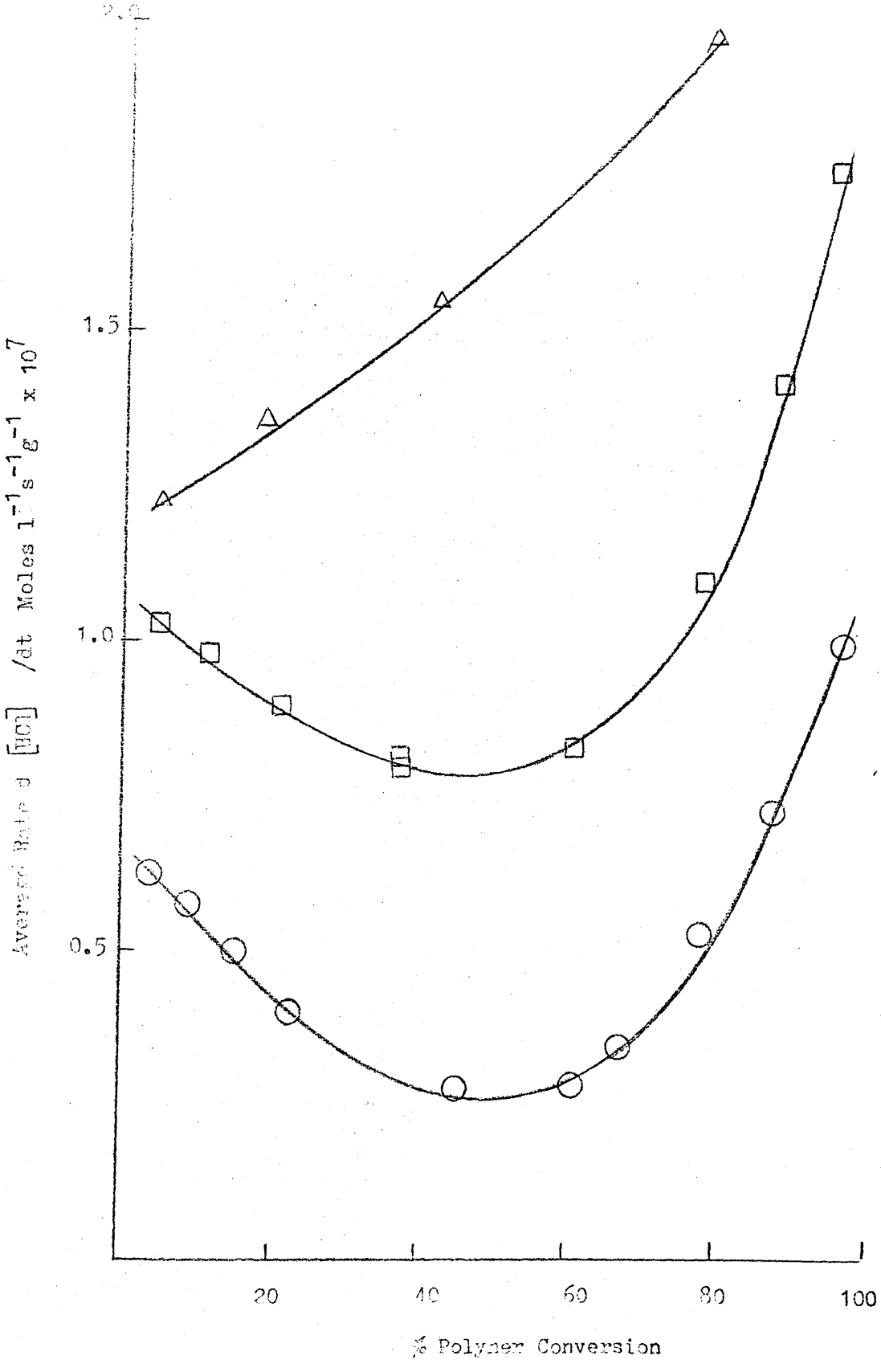


Fig. 4-17 EFFECT OF AIBN INITIATOR CONCENTRATION ON THE THERMAL STABILITY OF PVC POLYMERISED AT 60°C FOR DIFFERENT % CONVERSIONS
(From top to bottom 1.0M%, 0.1M% and 0.01 M%)

show the same relation with regards to three different initiator concentrations for Bz_2O_2 and AIBN respectively. The effect of different polymerisation temperatures on conversion was shown in figures 4-1, 4-2, 4-7, 4-8 and 4-9.

From these results it is evident that the nature of the variation of thermal stability with conversion to polymer is dependent on the initiator type, concentration and polymerisation temperature. In all the thermal, bulk polymerisation the plot of rate at different polymer conversions gave a 'trough' pattern having a minima for d [HCl] /dt at a medium conversion varying between 40 and 60%. This shallow peak would flatten out at high initiator concentrations and temperatures above 100°C or below 0°C.

Table 4-10 shows the minima at 38% conversion 0.01 M% Bz_2O_2 polymer with an increase of almost 1.75 fold in instability at the lowest conversion of 4% and an instability increase of 3 fold with the highest conversion of 96%. The same occurs with AIBN but with a much deeper valley, the polymer at low conversion (4%) being 2.25 more unstable and the one at high conversion (96.5%) being 3.6 fold more unstable.

The change of inhibition time with conversion is not of great magnitude, thus, we see in the same table, a change of only 20% for both Bz_2O_2 and AIBN, the longest inhibition periods coinciding with the most stable polymer conversions.

Based on the above results and the extent of decreased stability at low conversions; there must exist structures that are more unstable than chain ends and double bonds to bring about this effect. Branching might also be more prevalent than previously thought. It is also evident that at low conversions the instability of the polymer is so advanced that it is less effected by changes in temperature or initiator concentration than at high conversions. Followed probably by a process

Table 4-10. Effect of Polymerisation Conversion on the Thermal Stability of PVC at 60°C using 0.01 M% Initiator

Initiator 0.01 M%	Polymer % Conversion	Total Average Rate d [HCl]/dt Moles $l^{-1}s^{-1}g^{-1}$	Ratio d[HCl]dt to Lowest Rate	Inhibition Time (Mins.)	Ratio of Inhibition Time to Lowest Period
Bz_2O_2	4.3	0.66	1.74	16.0	1.14
	22.7	0.50	1.32	16.5	1.18
	25.7	0.43	1.13	17.0	1.21
	37.8	0.38	1.00	17.0	1.21
	63.5	0.62	1.63	16.0	1.14
	65.5	0.63	1.66	16.5	1.18
	74.5	0.79	2.08	15.5	1.1
	80.8	0.88	2.32	15.5	1.1
	96.0	1.14	3.00	14.0	1.0
AIBN	4.0	0.63	2.25	16.0	1.10
	8.9	0.58	2.07	16.5	1.14
	15.0	0.50	1.79	17.0	1.17
	22.5	0.40	1.43	17.0	1.17
	44.9	0.28	1.00	17.5	1.21
	61.0	0.28	1.00	17.5	1.21
	67.5	0.34	1.21	17.0	1.17
	78.0	0.53	1.89	16.5	1.14
	87.5	0.73	2.61	15.5	1.07
	96.5	1.01	3.61	14.5	1.0

of mopping up of radical producing unstable polymer. All of which indicates that there is more instability being created at low conversions. This unstable polymer is then diluted with more stable polymer as conversion progresses.

A hypothetical breakdown of the dehydrochlorination reaction into its probable segments is shown in fig. 4-18. Starting with an unstable polymer which increases its stability with conversion reaching a maximum at about 50%, then a second phase occurs where a highly stable polymer decreases in stability as conversion increases.

The nature of the unstable species at low conversion could be due to formation of double bonds, due to chain scission either based on the theory presented earlier or due to traces of oxygen or impurities such as acetylene or butadiene. Butadiene could copolymerise at the double bonds with the allylacitivity on the hydrogen forming a 1.4 addition adjacent to a hydrogen especially if molecular elimination of HCl is occurring. However, this seems to be an unlikely situation since stability is increased by the further reaction of double bonds produced. The increase in stability that follows could be an attack of the radicals on the double bonds or just a plain mopping up effect in conjunction with dilution with stable polymer. This would explain the flattening of the curve with higher initiator concentrations.

The weaknesses at high conversions would be due to more branching and formation of tertiary chlorides probably caused by increase in initiator concentration, or more unreacted initiator in the monomer phase or by the local adsorbed initiator on the polymer surface.

Thermal Stability of Photopolymerised PVC:

The results obtained for photo initiated PVC are shown in figure 4-19, Bz_2O_2 polymer is more stable than AIBN polymer by about three folds over the range of about 5 to 40% conversion.

The important feature is the absence of the 'trough' pattern seen in bulk polymerised PVC. Thus the photoinitiated polymer starts from a level of stability at low conversion and decreases in stability with increase in conversion. This decrease in stability over a range to

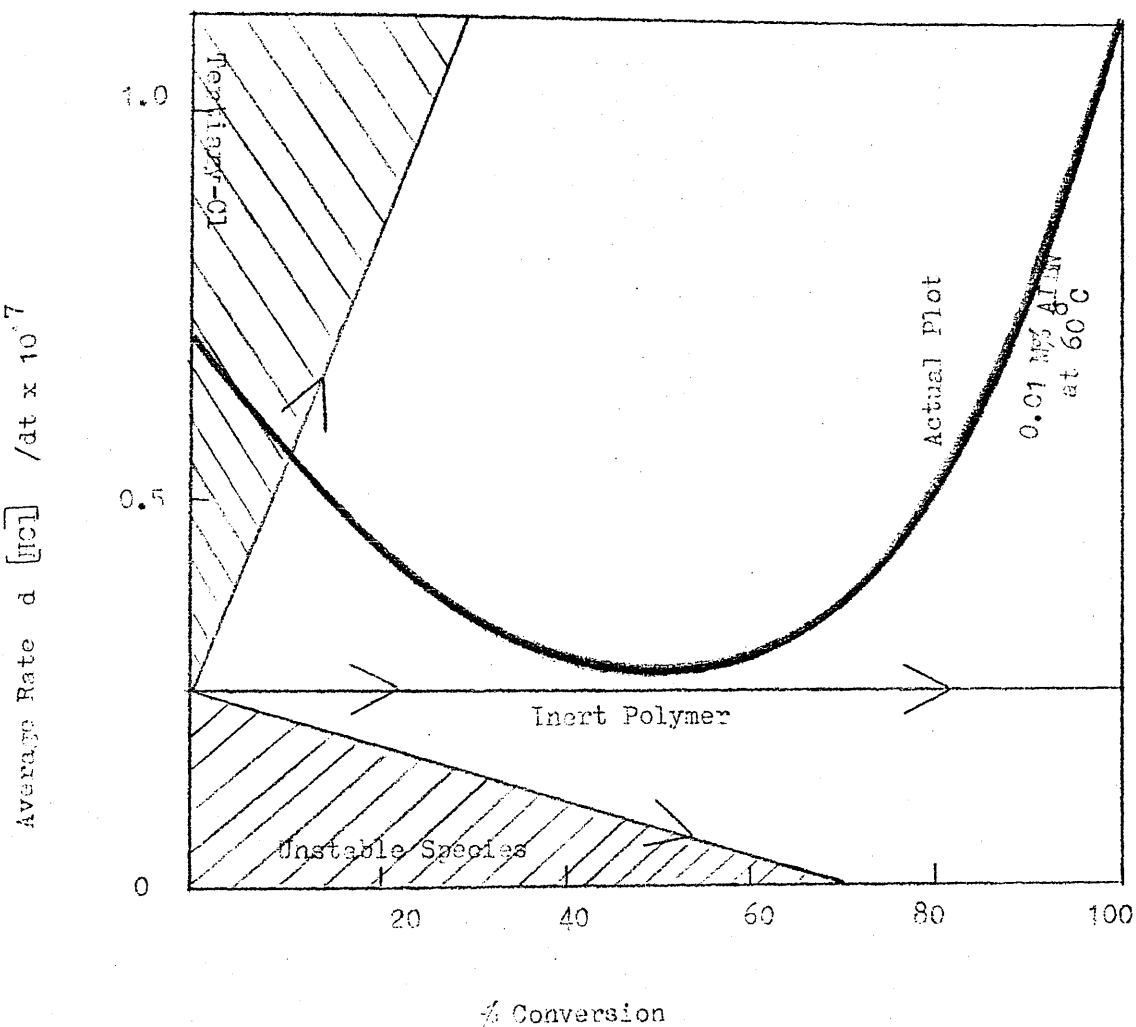


Fig. 4-18 BREAKDOWN OF DEHYDROCHLORINATION CURVE INTO PROBABLE COMPONENTS

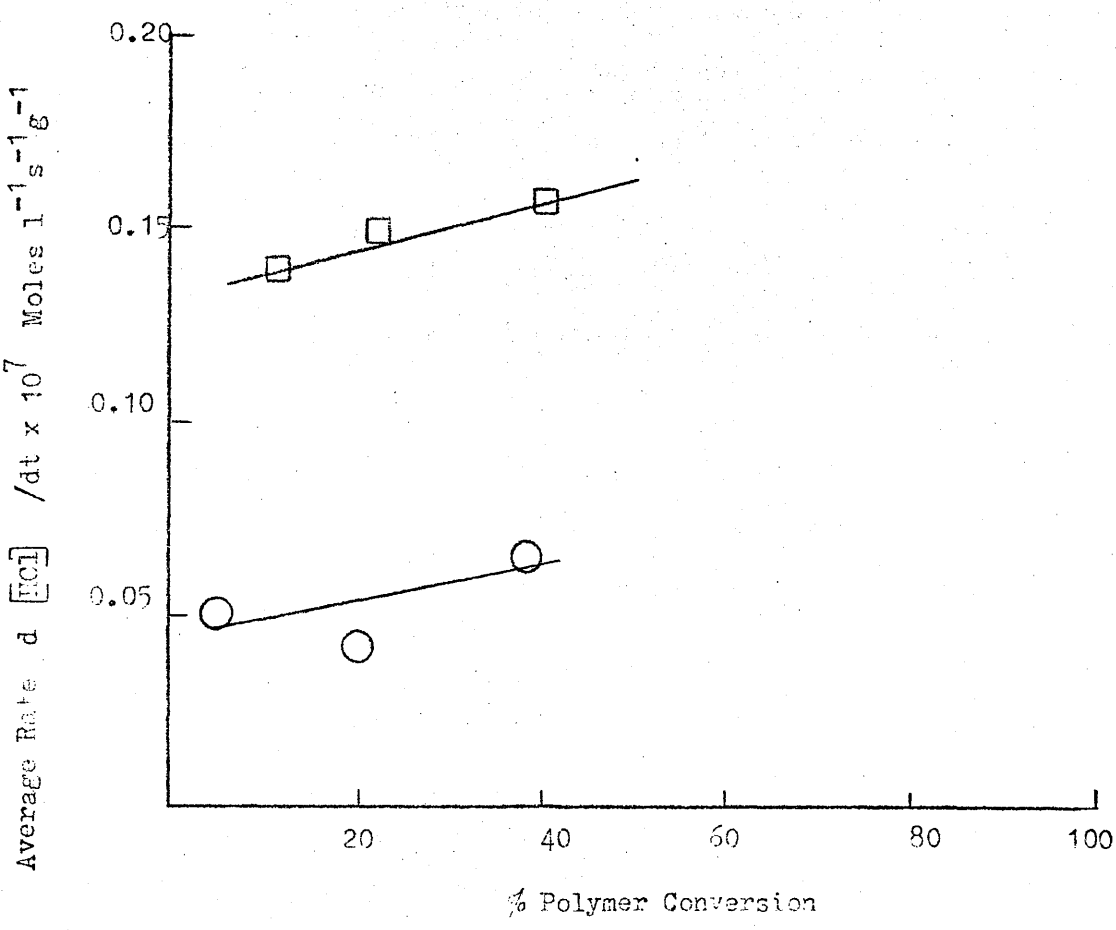


Fig. 4-19 EFFECT OF INITIATOR TYPE Bz_2O_2 —○○— AND AIBN —□□— THERMAL STABILITY OF PVC PHOTOPOLYMERISED AT 25°C USING 0.01 M% CONCENTRATION.

40% conversion is about 30% for Bz_2O_2 and only 12% for AIBN. This change is much less than what occurred with bulk polymers. A comparison of the thermal stability of photo initiated and thermal initiated Bz_2O_2 polymers is shown in Fig. 4-20. The level of stability of the photoinitiated polymer seems to be running at the 'minima' level of the thermal initiated polymers.

What could be happening is the peroxide impurities incorporated in polymer molecules are photodecomposed and break at the peroxide link to produce free radicals chains which further produce stable polymers.

Fig. 4-21 shows the change of thermal stability of photoinitiated PVC using 2 different initiator concentrations and zero concentration. The fact that it was able to polymerise vinyl chloride without an initiator leaves us in doubt. The dehyrochlorination rate obtained for such a polymer was 0.0 Moles $l^{-1}s^{-1}g^{-1}$ for a 10% conversion, over a one hour degradation period. The effect of increasing the initiator concentration at these low levels follow the same straight line relation seen with bulk polymers with higher initiator concentration.

Thermal Stability of PVC polymerised in the presence of diluents.

PVC prepared in different solvents and diluents at 60°C, as described in Chapter 3, was degraded in ethyl benzoate for 60 minutes at 198°C.

The results are shown in Table 4.11 in descending order of stability based on the amount of HCl liberated. The rate of dehydrochlorination of these polymers which are in the range of about 20% conversion varies about 8 fold over the series of solvents studied. Two solvents give remarkable stable polymers; methyl iodide and dichlorobutane. Their stability compares to that of bulk polymers prepared at lower temperatures i.e. 40 and 25°C.

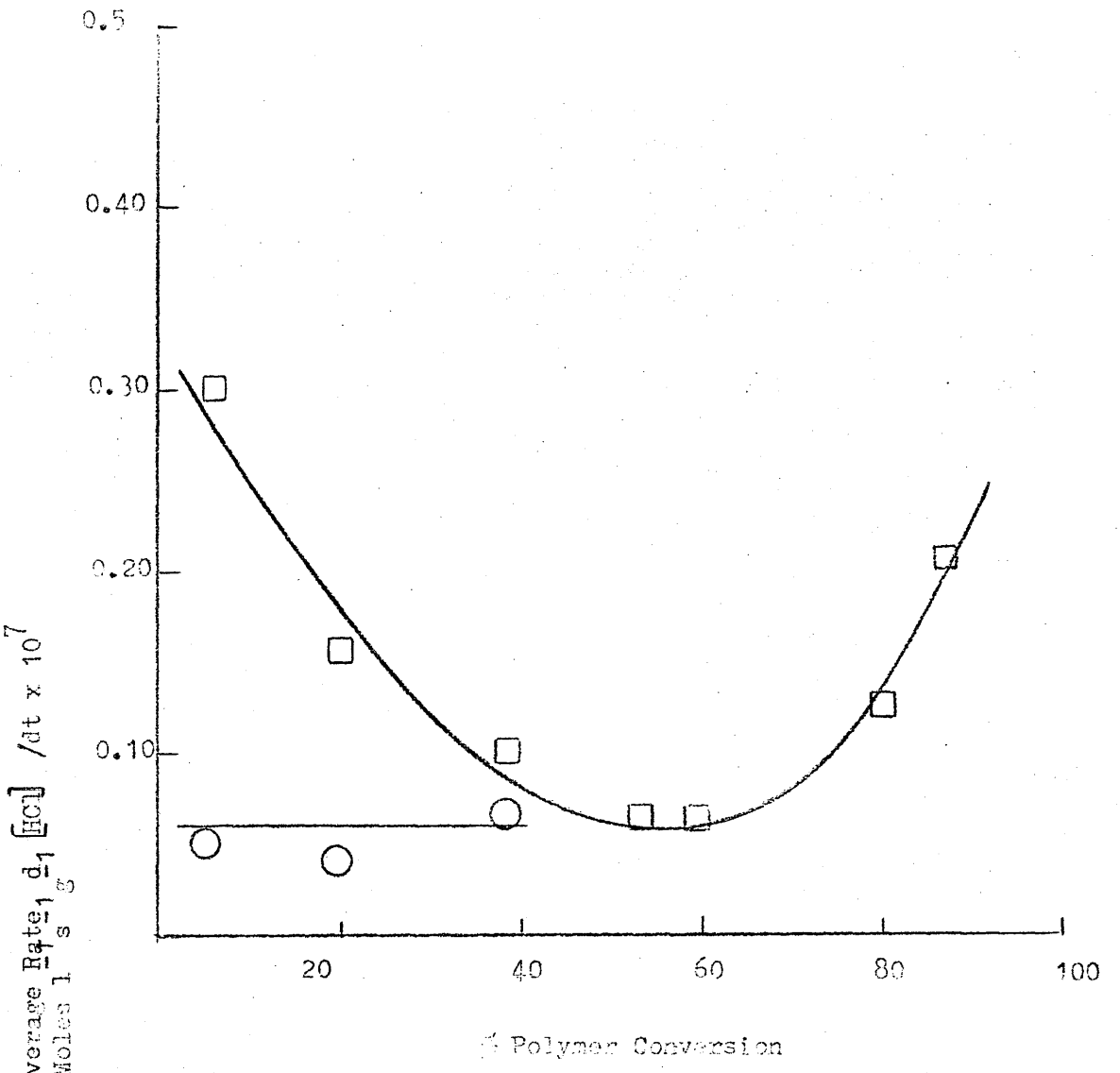


Fig. 4-20 COMPARISON OF THERMAL STABILITY OF PVC PREPARED BY PHOTOPOLYMERISATION —○—○— AND THERMAL POLYMERISATION —□—□— at 25°C AND 0.01 M% Bz_2O_2

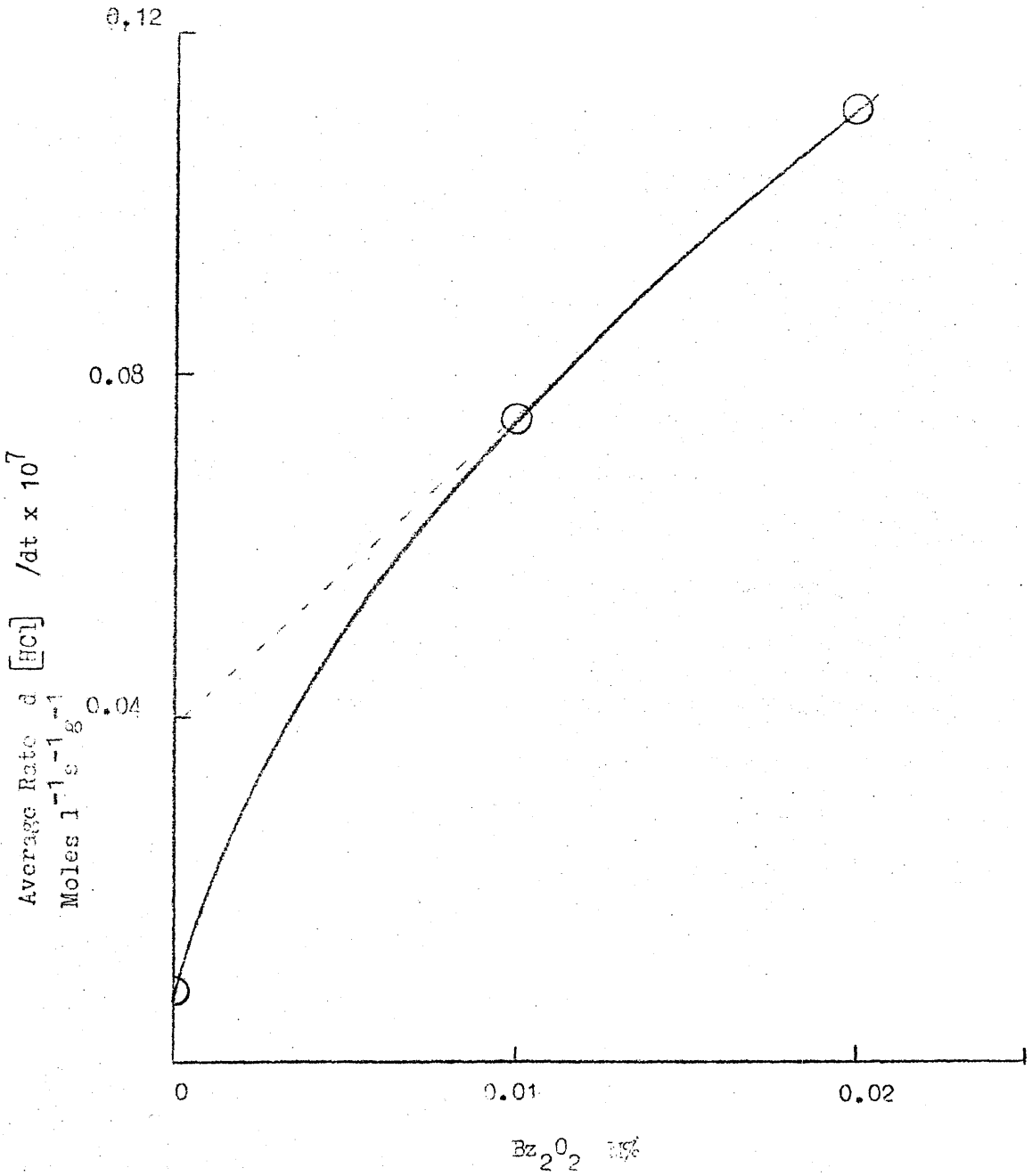


Fig. 4-21 EFFECT OF Bz_2O_2 INITIATOR CONCENTRATION ON THE THERMAL STABILITY OF PHOTOPOLYMERISED PVC AT 25°C TO ABOUT 10% POLYMER CONVERSION

The least stable polymers were those polymerised in the presence of tetrahydrofuran, cyclohexane, acet-dimethylamide, and DMF.

The intrinsic viscosities of all the polymers were on the low side varying from 0.10 to 0.48 and an $\overline{Mn}$ variation of 15,000 to 46,000. The lowest three intrinsic viscosities being the ones for diethyl phosphate, isopropyl benzene and tetrahydrofuran. The highest intrinsic viscosities were those for dioctyl phthalate, dibutyl phthalate, ethyl benzoate,dichlorobutane, chlorobenzene, bromobenzene and cyclohexane.

The inhibition times were roughly related to the rate of dehydrochlorination with the exception of cyclohexanone having a lower inhibition period and bromobenzene having a higher inhibition period relative to their rate of dehydrochlorination. The number of radicals per polymer chain was calculated from the specific activity of the polymers. Methyl iodide polymers show a very low number of radicals 2/100 while benzophenone being the other extreme with about 3 radicals per chain. The highest number of radicals excluding the previous two extremes occur in the case of dichlorobutane, ethyl benzoate bromobenzene and dibutyl phthalate, all of which have about one radical per chain. The minimum number of radicals per chain occurred with, tetrahydrofuran, acet-dimethylamide, dimethyl formamide and diethyl phosphate, all having about one radical per 10 to 15 chains. The absorbance maxima at 370 m μ recorded after 60 minute degradation at 198^{o}C, follows the same trend as the rate of dehydrochlorination, except for methyl iodide which has one of the highest values. The spectrum of several polymers are shown in fig. 4-22, which also compares them with that of a polymer prepared in bulk and degraded for only 10 minutes. The solution polymers on the whole seem to be more stable to change in colour i.e. formation of polyene chains.

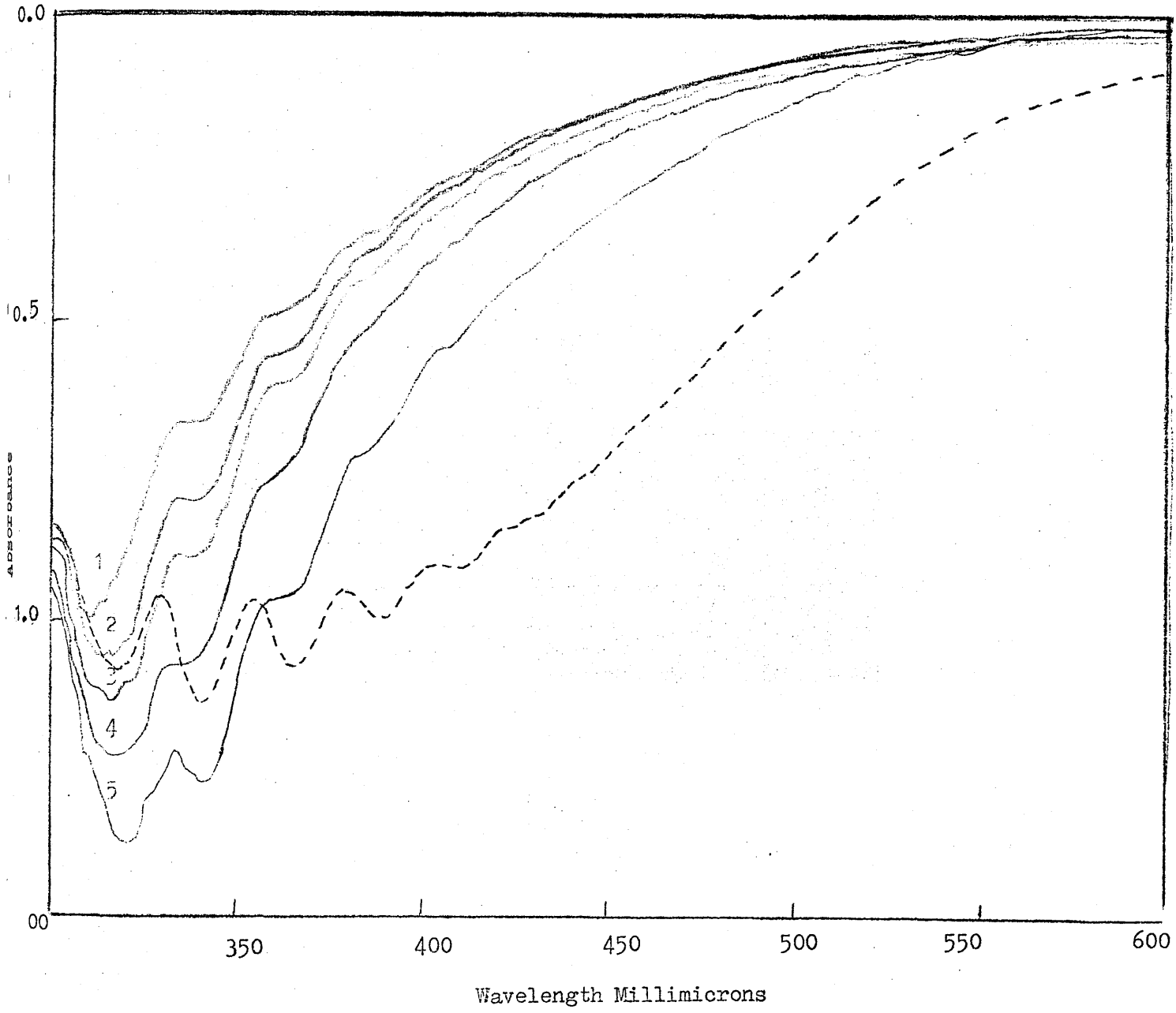


Fig. 4-22 ABSORBTION SPECTRUM OF SOLUTION POLYMERS OF 1 - Ethyl Benzoate 2 - Tetrahydrofuran 3 -Diethyl phosphate 4 - Tritolyl phosphate 5 - Cyclohexane
After 60 minutes Degradation in Ethyl Benzoate at 198°C
Broken curve, is for Bulk Polymer after 10 minutes Degradation

Table 4.11. Effect of Polymerisation Diluents on the Thermal Stability of PVC

Diluent	Intrinsic Viscosity	$\overline{Mn} \times 10^3$	Number of Radicals/ Polymer Chain	Inhibition Time (Mins.)	Total Average Rate $d[HCl]/dt \times 10^7$ Moles $l^{-1}s^{-1}g^{-1}$	Absorbance at 370 mμ after Degradation
Methyl iodide	0.23	25.0	0.02	21.0	0.19	1.35
Dichlorobutane	0.43	43.0	1.40	20.0	0.28	0.99
Ethyl benzoate	0.47	44.0	1.06	22.0	0.44	1.0
Cyclohexanone	0.19	22.5	0.37	7.5	0.44	1.05
Epoxyoctyltallate	0.32	32.0	0.35	17.0	0.50	1.09
Chlorobenzene	0.42	40.0	0.74	14.0	0.53	1.02
Benzophenone	0.26	27.8	2.68	12.5	0.58	1.1
Bromobenzene	0.39	37.0	0.85	21.5	0.64	1.1
Isopropylbenzene	0.16	20.0	0.47	12.5	0.67	1.06
Dioctylphthalate	0.48	44.6	0.59	17.0	0.69	
Dibutylphthalate	0.50	46.0	0.93	15.0	0.72	1.1
Diethylphosphate	0.10	15.5	0.16	15.0	0.75	1.15
Tritolyphthalate	0.25	27.0	0.62	17.0	0.78	1.25

Table 4.11 Effect of Polymerisation Diluents on the Thermal Stability of PVC

Diluent	Intrinsic Viscosity	$\overline{Mn} \times 10^3$	Number of Radicals/ Polymer Chain	Inhibition Time (Mins.)	Total Average Rate $d[HCl]/dt \times 10^7$ Moles $l^{-1}s^{-1}g^{-1}$	Absorbance at 370 m after Degradation
Tetrahydrofuran	0.17	21.0	0.10	18.5	0.81	1.07
Dimethyl formamide	0.24	26.3	0.13	11.0	0.62	
Cyclohexane	0.39	36.0	0.29	12.5	1.11	1.38
Acet-dimethlyamide	0.27	28.5	0.12	12.0	1.47	1.35

They all show the same discrete peaks associated with PVC, at about 365, 390, 415 and 480 mμ . Fig. 4-23 shows the relation of % conversion to rate of dehydrochlorination for PVC prepared in the presence of DMF. It is noticed that the profile of the curve is different than that for bulk polyners. There is a decrease of stability with increase in conversion up to about 20% when the curve reaches a plateau. It is interesting to note, that with the exception of methyliodide - PVC polymers, the dichlorobutane and ethyl benzoate polymers which are the most stable also have the highest molecular weight and number of radicals per chain.

Most of the high molecular weight plasticisers are grouped in one category with higher inhibition periods than anticipated and medium stability. PVC, prepared in the presence of solvents, has a greatly reduced molecular weight depending on the extent of chain transfer to solvent reactions and consequently the effect of the chain end will be of greater importance when discussing the thermal stability of the polymers thus formed. As chain transfer to solvent is non degradative and is obviously so important, a vast number of polymer chains will have terminal groups derived from the solvent. The extent of the effect of these terminal groups can be studied by varying the monomer concentration.

In general, the rates of dehydrochlorination would seem to depend on the exact nature of the solvent present and its ability to act as a chain transfer agent with some very interesting clues for further study.

The Effect and Changes of Molecular Weight During the Degradation of PVC

The changes that occur in the molecular weight are dependant on the initial values and the different polymerisation conditions. Intrinsic viscosities were measured before ($[\eta]_0$) and after 60

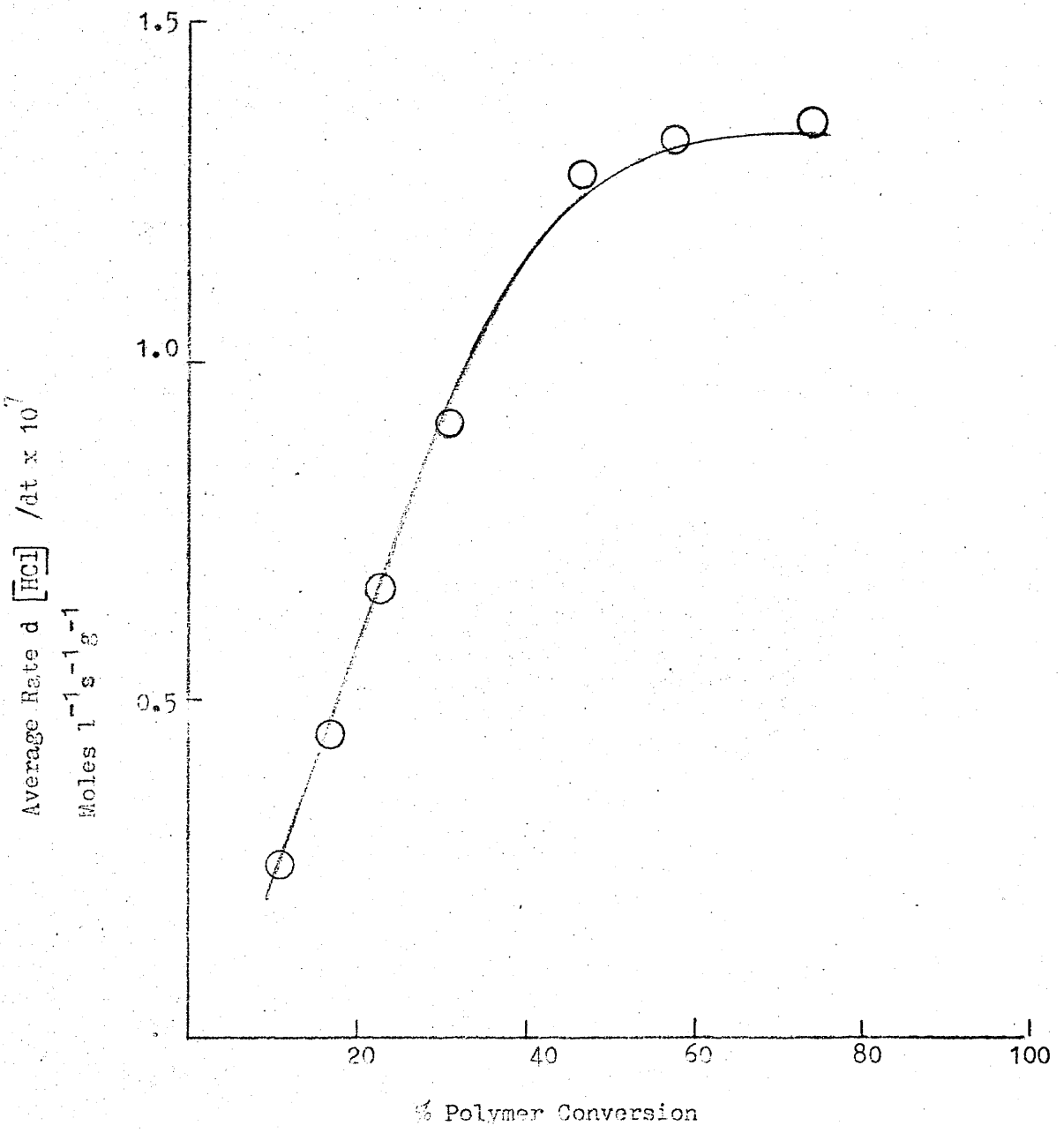


Fig. 4-23 DEHYDROCHLORINATION CURVE FOR PVC POLYMERISED IN DMF

minutes degradation at 198°C $\left([\eta]_D\right)$. Table 4.12 shows such changes for low conversion polymers. The intrinsic viscosity increases with degradation for all three initiator concentrations of Bz_2O_2. With AIBN chain scission occurs for the same initiator concentrations. The ratio of change in viscosities with Bz_2O is highest for the highest initiator concentration, while the lowest is for the medium concentration of 0.10 M%. AIBN shows the highest change for the lowest initiator concentration. Table 4.13 shows the same effect for medium conversions. The ratio of viscosities is lower than in low conversions for Bz_2O_2, but almost the same for AIBN polymers. AIBN initiated polymers still show a chain scission. At high conversions Table 4.14, Bz_2O_2 polymers follow the same trend as the lower conversions with cross linking being more advanced for the low and high initiator concentration. AIBN initiated polymers at 0.01 and 0.10 M% undergo cross linking at this conversion while for 1.0 M% a decrease in viscosity is still evident. The greatest changes occur at low conversions which would indicate that polymers at low conversions are more likely to cross link (in the case of Bz_2O_2) or undergo scission (in case of AIBN), reflecting the strong influence of initiator concentration. The fact that at high conversion both polymers cross link, could be due to the added effect of cross linking through branching. At low conversion the cross linking of the Bz_2O_2 initiated polymers could be due to (a) the initial molecular weight which is lower than that of AIBN initiated polymer or (b) to the faster rate of dehydrochlorination of the AIBN initiated polymers or (c) the peroxide fragments being more effective in recombining chains. Fig. 4.24 shows how in the case of Bz_2O_2 the change in viscosity increases with higher initiator concentration while the reverse occurs with AIBN initiated polymers to 60% conversion, polymerised at 60°C. Table 4.15 relates the

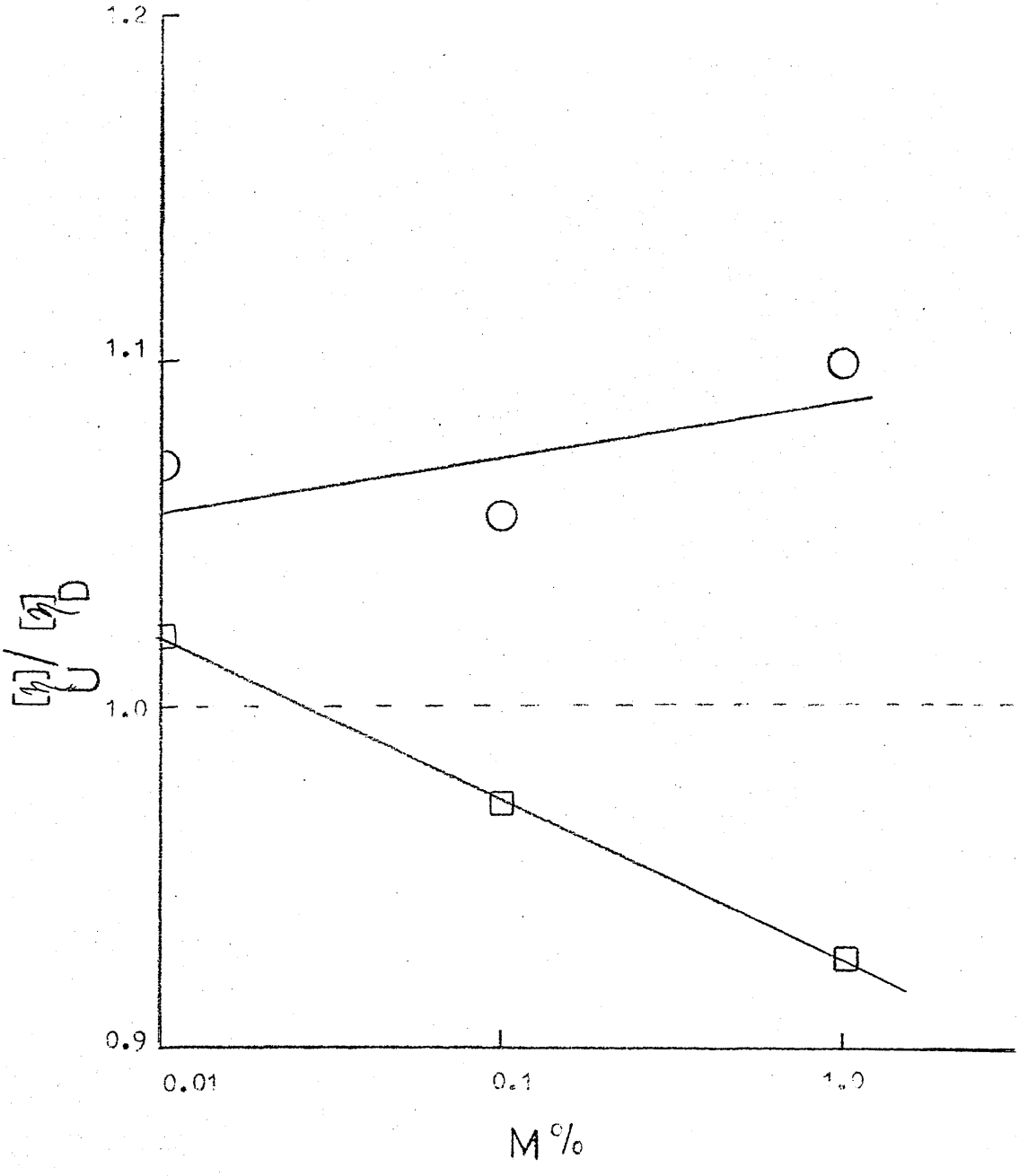


Fig. 4-24 EFFECT OF INITIATOR CONCENTRATION ON CHANGE OF VISCOSITY AFTER DEGRADATION FOR 60% CONVERSION POLYMER INITIATED BY Bz_2O_2 —○-○— and AIBN -□-□-

Table 4.12. Effect of Initiator Type and Concentration on the viscosity after degradation of PVC prepared at 60°C for low polymer % Conversion

Initiator and Concentration M%	Polymer % Conversion	$[\eta]_u$ Undegraded	$[\eta]_d$ Degraded	$[\eta]_d / [\eta]_u$	$d[HCl]/dt$ Moles $l^{-1}s^{-1}g^{-1}$ x 10^7
Bz_2O_2 :					
0.01	4.3	0.65	0.78	1.20	0.66
0.10	7.0	0.56	0.62	1.11	0.70
1.0	4.8	0.47	0.58	1.23	0.87
AIBN :					
0.01	4.0	0.73	0.72	0.99	0.62
0.10	4.3	0.70	0.58	0.83	1.03
1.0	5.3	0.65	0.54	0.83	1.23

Table 4.13. Effect of Initiator Type and Concentration on the Viscosity after Degradation of PVC prepared at 60°C for medium polymer % Conversion

Initiator and Concentration M%	Polymer % Conversion	$[\eta]_u$ Undegraded	$[\eta]_d$ Degraded	$[\eta]_d / [\eta]_u$	$d[HCl]/dt$ Moles $l^{-1}s^{-1}g^{-1}$ x 10^7
Bz_2O_2 :					
0.01	37.8	0.75	0.80	1.07	0.38
0.10	41.8	0.67	0.69	1.03	0.61
1.0	42.0	0.58	0.66	1.14	1.14
AIBN :					
0.01	44.9	0.79	0.79	1.0	0.28
0.10	37.0	0.74	0.69	0.93	0.79
1.0	41.9	0.71	0.63	0.89	1.57

Table 4.14. Effect of Initiator Type and Concentration on the Viscosity after Degradation of PVC prepared at 60°C for High Polymer % Conversion

Initiator and Concentration M%	Polymer % Conversion	$[\eta]_u$ Undegraded	$[\eta]_d$ Degraded	$[\eta]_d/[\eta]_u$	$d[HCl]/dt$ Moles $l^{-1}s^{-1}g^{-1}$ x 10^7
Bz_2O_2 :					
0.01	96.0	0.92	0.99	1.08	1.14
0.10	90.0	0.80	0.83	1.04	1.41
1.0	94.2	0.72	0.79	1.10	1.58
AIBN :					
0.01	96.5	0.86	0.90	1.05	1.01
0.10	95.5	0.82	0.87	1.06	1.81
1.0	93.6	0.78	0.75	0.96	2.12

effect of polymerisation temperatures to molecular weight changes during degradation. The initial molecular weight decreases with decreasing polymerisation temperatures. The change in viscosity is again most prominent with low conversion polymers. The results also indicate that for polymers prepared at low temperature of 25 and 40°C a chain scission reaction predominates while at 60 and 80°C it is a cross linking reaction, this becomes evident in Fig. 4-25.

This would be expected due to the greater likliehood of branching in high temperature polymerisations. The second trend is one of decreasing in the viscosity change with increase in conversion for polymers prepared at 60 and 80°C and an increase in the viscosity ratio with the 40 and 25°C prepared polymers. Table 4.16 shows the change of viscosity due to degradation for polymers prepared at high temperatures. The initial molecular weights are relatively low and they all undergo cross linking at a much faster rate, as reflected by the higher intrinsic viscosity ratios. Some increasing by 3 fold,

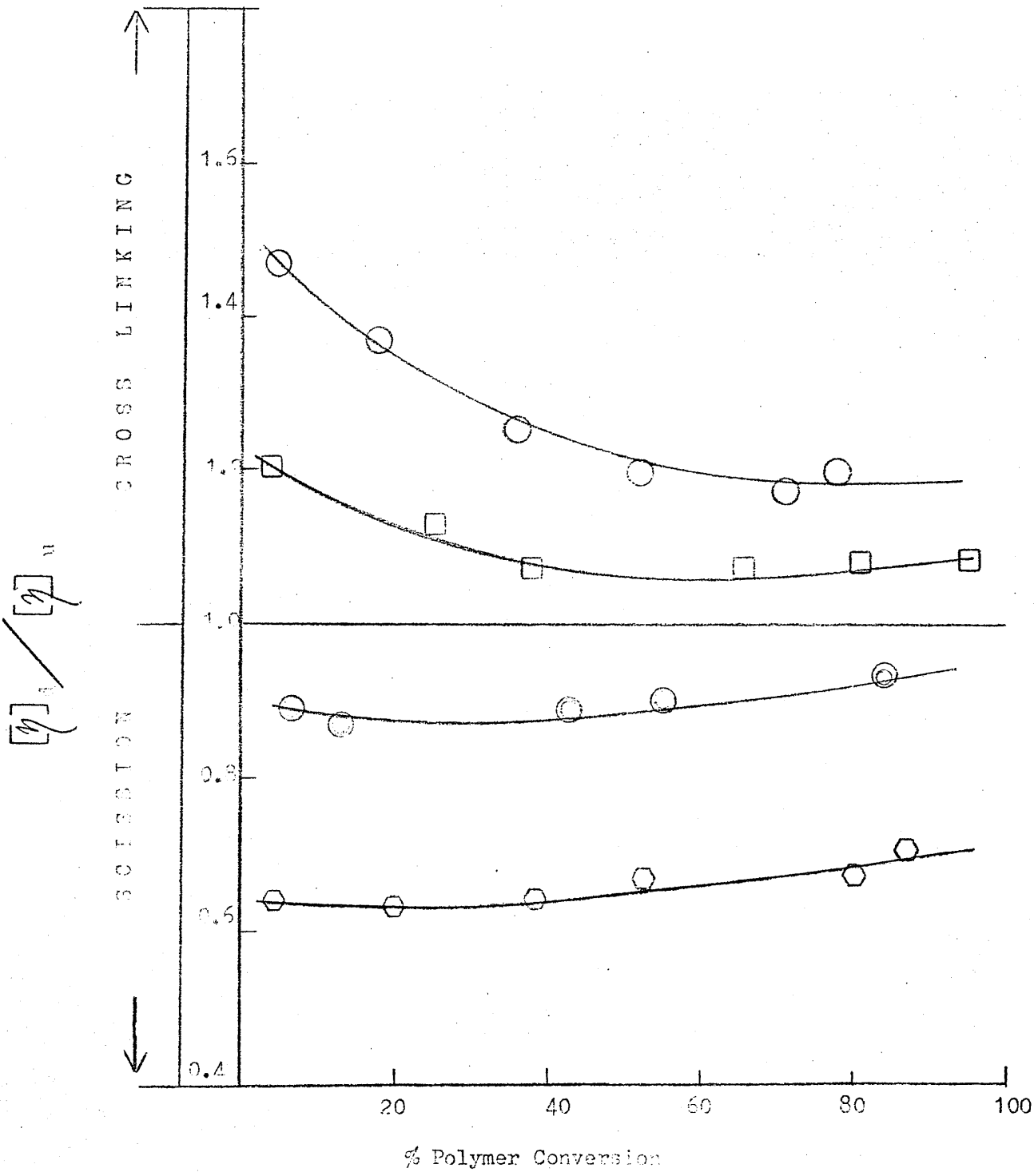


Fig. 4-25 CHANGES IN VISCOSITY AFTER DEGRADATION AS RELATED TO POLYMERISATION TEMPERATURE USING PVC POLYMERISED WITH 0.01 M% (From top to bottom 80°C, 60°C, 40°C and 25°C)

Table 4.15. Effect of Polymerisation Temperature on the Viscosity Change of Degraded PVC (PVC polymerised with 0.01 M% Bz_2O_2 initiator)

Polymerisation Temperature °C	Polymer % Conversion	$[\eta]_u$ Undegraded	$[\eta]_d$ Degraded	$[\eta]_d / [\eta]_u$	$d[HCl]/dt$ Moles $l^{-1}s^{-1}g^{-1}$ x 10^7
High Conversions :					
25	86.5	2.58	1.8	0.70	0.21
40	84.0	1.50	1.40	0.93	0.47
60	80.8	0.87	0.94	1.08	0.88
80	78.0	0.52	0.62	1.19	2.08
Medium Conversions :					
25	38.5	2.35	1.50	0.64	0.10
40	43.0	1.40	1.24	0.89	0.13
60	37.8	0.75	0.80	1.07	0.38
80	43.0	0.44	0.55	1.25	1.19
Low Conversions :					
25	4.2	2.17	1.39	0.64	0.3
40	6.7	1.30	1.15	0.88	0.42
60	4.3	0.65	0.78	1.20	0.66
80	4.7	0.34	0.48	1.41	1.14

the higher changes being associated with higher polymer conversions.

Table 4.17 shows the intrinsic viscosity relation to the degradation of polymers prepared at low temperatures. The change in intrinsic viscosity is the greatest in this temperature range, with a drop of about 20 fold in the case of polymer prepared at 0°C. This is expected, since the breaking of few bonds in a high molecular weight polymer will have a much greater effect than in the case of a low molecular weight one.

Table 4.16. Effect of high Temperature of Polymerisation on the Viscosity of Degraded PVC, Polymerised using 0.1 M% Bz_2O_2.

Polymerisation Temperature °C.	Polymer % Conversion	$[\eta]_u$ Undegraded	$[\eta]_d$ Degraded	$[\eta]_d / [\eta]_u$	d[HCl]/dt Moles $l^{-1}s^{-1}g^{-1}$ x 10^7
100	28.3	0.15	0.27	1.80	2.11
	62.5	0.29	0.35	1.21	3.38
	72.5	0.30	0.43	1.43	4.75
120	2.8	0.11	0.16	1.45	1.90
	26.6	0.14	0.36	2.57	4.00
	37.2	0.16	0.47	2.94	6.57
140	10.8	0.08	0.14	1.75	2.90
	18.0	0.09	0.18	2.00	4.75
	38.4	0.12	0.33	2.75	12.67

Table 4.17. Effect of Low Temperature of Polymerisation on the Viscosity after degradation of PVC, Polymerised using 0.01 M% AIBN.

Polymerisation Temperature °C.	Polymer % Conversion	$[\eta]_u$ Undegraded	$[\eta]_d$ Degraded	$[\eta]_d / [\eta]_u$	d [HCl]/dt Moles $l^{-1}s^{-1}g^{-1}$ x 10^7
0	20.3	2.2	0.10	0.05	0.033
- 25	22.2	2.5	0.34	0.14	0.023
- 50	19.6	3.6	1.08	0.30	0.015
- 75	18.0	Insoluble	Insoluble	-	0.010

The effect of polymerisation conversion is shown in Table 4.18 covering a range of 4 to 95%. Fig. 4-26 and 4-27 illustrate this relation.

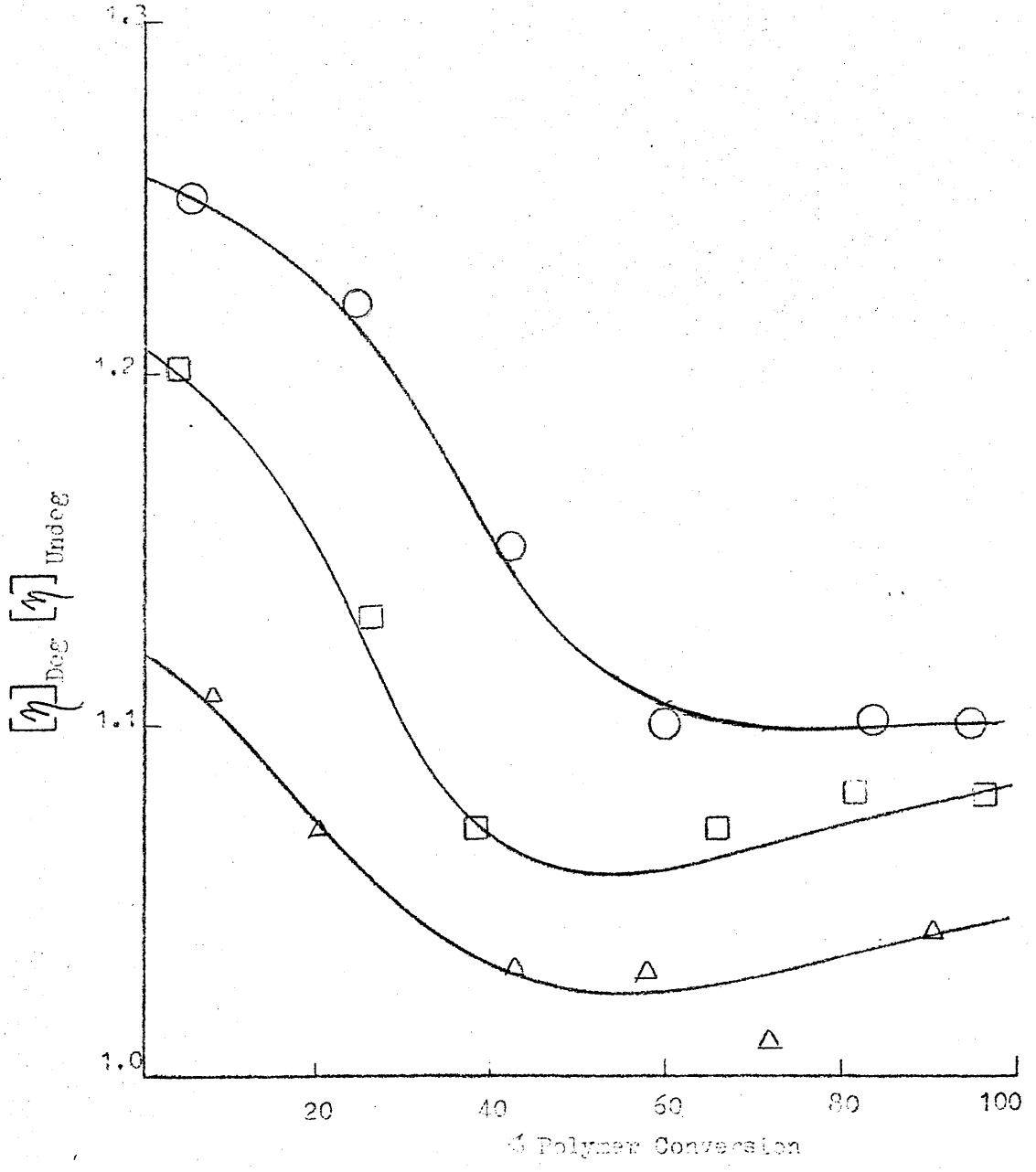


Fig. 4-25 CHANGES IN VISCOSITY AFTER DEGRADATION AS RELATED TO POLYMER CONVERSION FOR PVC POLYMERISED WITH H_2O_2 at 60°C
(From top to bottom 1.0%, 0.01 M% and 0.10 M%)

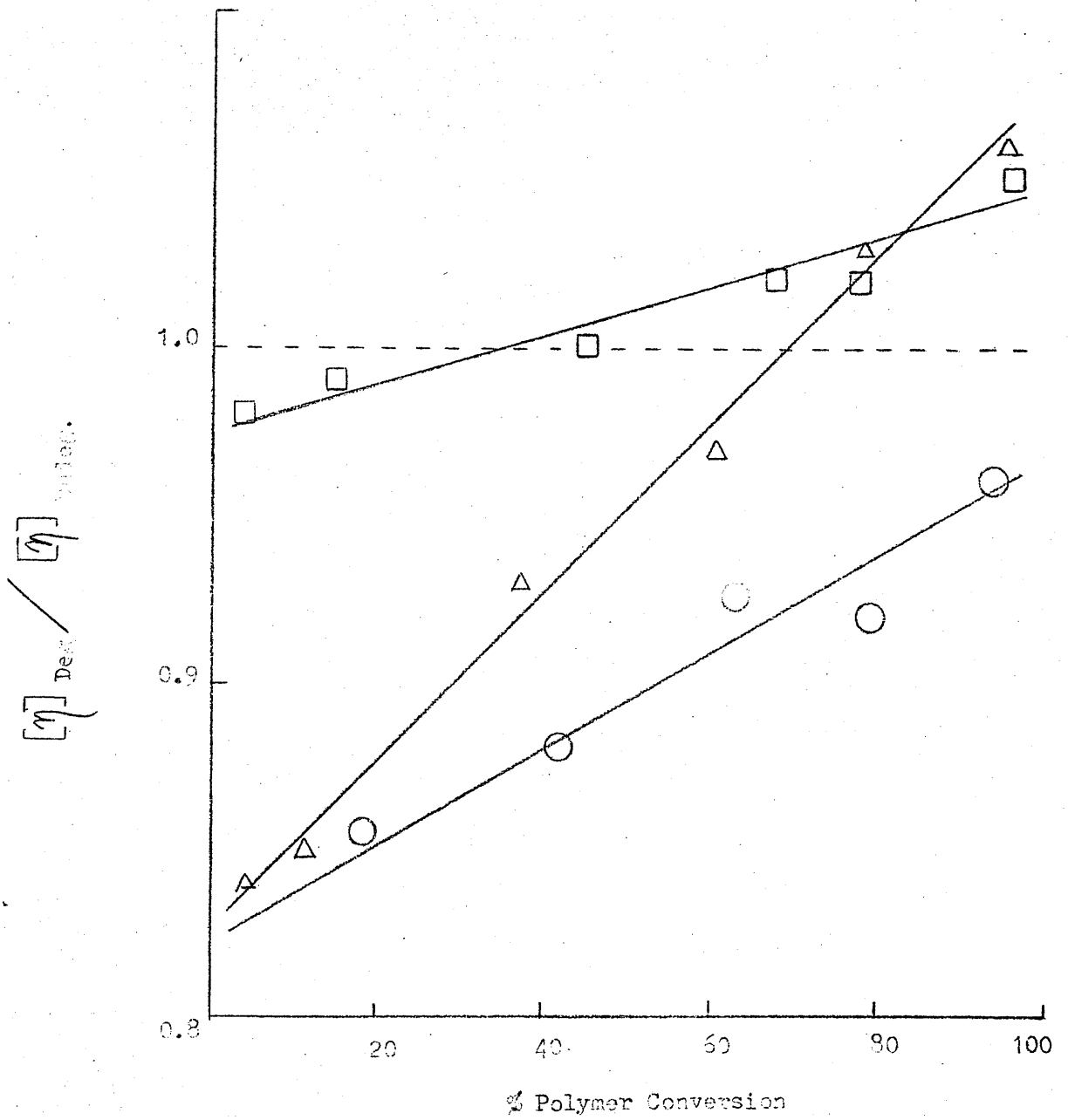


Fig. 4-27 CHANGES IN VISCOSITY AFTER DEGRADATION AS RELATED TO POLYMER CONVERSION POLYMERISED WITH AIBN AS INITIATOR AT 60°C. —○—○— 1.0 M%; —△—△— 0.1 M%, —□—□— 0.01 M%

In the case of Bz_2O_2 initiated polymers for all three concentrations, there is a decrease in the intrinsic viscosity ratio with increase in conversion up to about 50% conversion, then the change levels off. In all cases it is a cross linking reaction which occurs. The greatest change being one of 20% increase in viscosity for a 4% conversion polymer. In the case of AIBN Fig. 4-27 there is no similar trend, actually, there seems to be no trend at all, and a greater scatter of points. The change in intrinsic viscosity seems to increase with conversion. The great rate of change being for the 0.1 M% initiated polymer.

Figure 4.28 is a plot of the simultaneous dehydrochlorination reaction and the change in viscosity as discussed in the beginning of this chapter. The intrinsic viscosity drops by about 25% initially and then increases by a slow rate followed by a very fast rate when it is increased by three fold and reaches a plateau and continues to increase at a very slow rate.

Tracer Studies on the Degradation of PVC

The PVC initiated with Carbon^{-14} Labelled initiator was degraded for 60 minutes at 198^{o}C then the activity was counted using the liquid scintillation technique as described in Chapter 2, to determine the changes occurring at the initiator end fragments.

A total loss of the activity was experienced in all cases. On repeating the degradation for shorter times, the counts were found to drop sharply within 10 minutes Fig. 4.29 . After investigation, it was concluded that this was due to the presence of polyene chains in the degraded polymer. Even traces of these chromophores had a 'quenching' effect on the photons, i.e. they are absorbed by the degraded polymer solution and do not reach the photo multiplier tube. To overcome this difficulty it was necessary to pyrolyse the polymer

FIG. 4-28 CHANGES IN VISCOSITY (PROPER TIME) DURING THE DEHYDROCHLORINATION (SOLID LINE —●—●—●—) AND OXIDATION (—O—O—O—) OF PVC AT 199°C IN SOLUTION

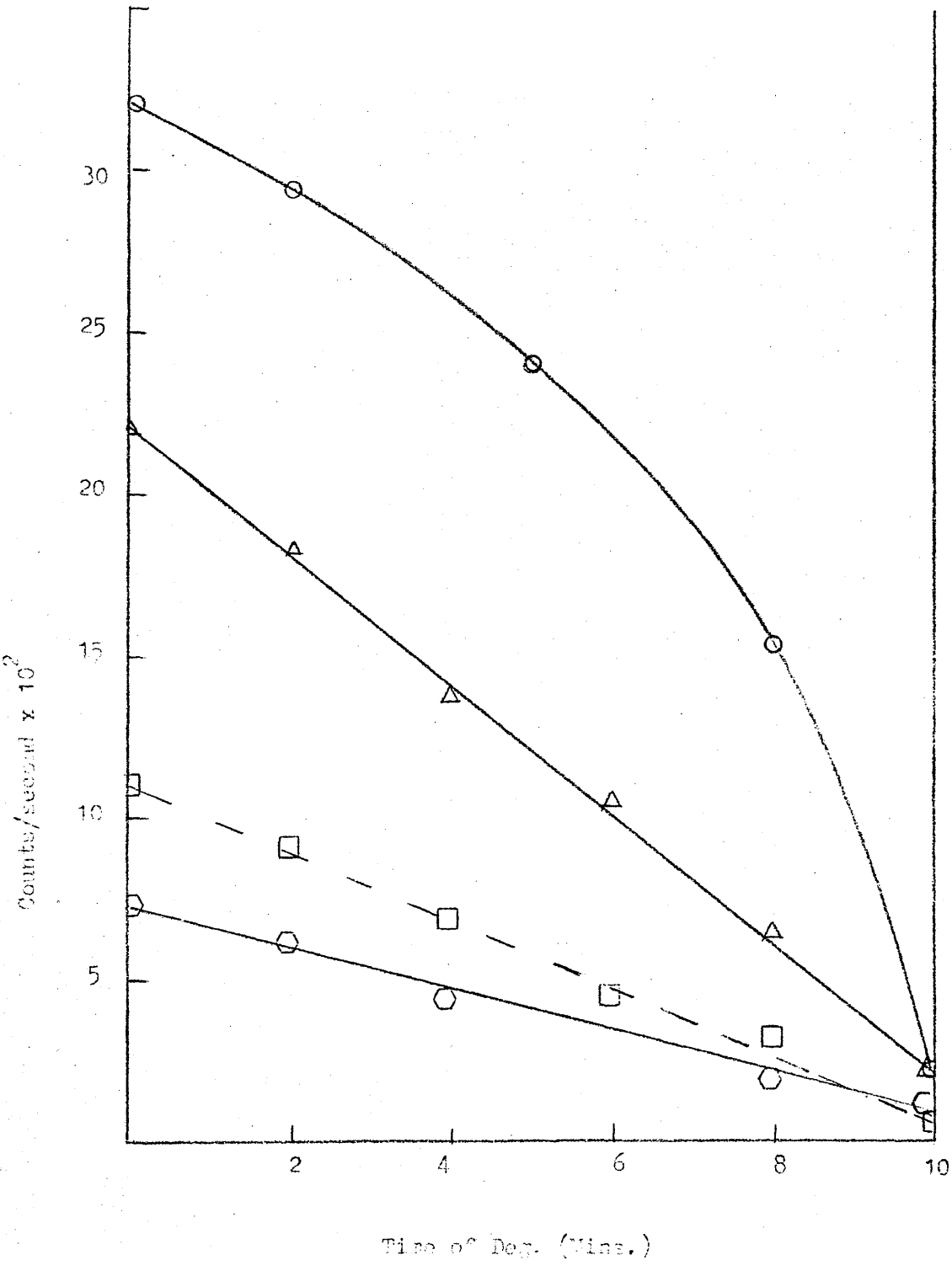


Fig. 4-29 EFFECT OF DEHYDROCHLORINATION AT 198°C ON C^{14} LABELLED PVC
-⬡- 25°C polymer; -△- 60°C polymer 4.2% Conversion
-□-60°C polymer; 65 Conversion; -○- 120°C polymer

Table 4.18. Effect of Polymerisation Conversion on the Viscosity of degraded PVC Polymerised at 60°C using 0.01 M% Initiator

Initiator	Polymer % Conversion	$[\eta]_u$ Undegraded	$[\eta]_d$ Degraded	$[\eta]_d / [\eta]_u$	[d HCl]/dt Moles $l^{-1}s^{-1}g^{-1}$ x 10^7
Bz_2O_2	4.3	0.65	0.78	1.20	0.66
	22.7				0.50
	25.7	0.73	0.82	1.12	0.43
	37.8	0.75	0.80	1.07	0.38
	63.5				0.62
	65.5	0.82	0.88	1.07	0.63
	74.5				0.79
	80.8	0.87	0.94	1.08	0.88
	96.0	0.92	0.99	1.08	1.14
AIBN	4.0	0.73	0.72	0.99	0.63
	8.9				0.58
	15.0	0.75	0.74	0.99	0.50
	22.5				0.40
	44.9	0.79	0.79	1.00	0.28
	61.0				0.28
	67.5	0.80	0.86	1.08	0.34
	78.0	0.84	0.86	1.02	0.53
	87.5				0.73
	96.5	0.86	0.90	1.05	1.01

to carbon dioxide and absorb it in primene.

This colourless solution is then used for liquid scintillation counting.

The work repeated in this fashion[137] on only two samples showed that there was no significant drop in activity on degradation. This would

indicate that either catalyst end fragments have no effect on initiating degradation or that they do initiate but do not become detached from the polymer chain.

From the tracer work on the undegraded polymer it was possible to determine the kinetic chain length (KCL) and the number of radicals per chain .

The specific activity for AIBN was found to be 10600 counts sec^{-1} gr^{-1} and 6000 counts $sec^{-1}gr^{-1}$ for Bz_2O_2. By using the equation of specific activity of polymer/specific activity of initiator, it was possible to obtain the KCL. The number of radicals per chain was calculated by dividing the number average molecular weight $\overline{Mn}$ by the monomer molecular weight and the KCL.

Table 4.19 shows how activity is effected by initiator type and concentration. At low conversions the KCL for Bz_2O_2 initiated polymer is lower than the AIBN initiated polymers at both 0.10 and 0.01 M%. At higher conversions the trend seems to be the same. With increase in initiator concentration there is almost a three fold decrease in the KCL. The number of radicals per chain is more than doubled by increasing the initiator concentration by 10 fold, while molecular weight drops by almost half, therefore, the net activity per unit weight must increase by about 3.5 fold. At higher initiator concentrations, it seems to be more wasteful with relatively fewer fragments ending up in the polymer. This is probably due to inefficient initiation, where radicals terminate themselves or due to other side reactions. This would fit the thermal stability pattern which goes up by a factor of 3, while the number of fragments increases by 2 fold. Therefore, initiator fragments could still be important, especially at low conversions where we have a lot of unused fragments which contribute to instability and which could react again at higher conversions.

Table 4.19. Effect of Initiator type and Concentration on Thermal Stability of C^{14} Labelled PVC

Initiator and Concentration M%	Polymer % Conversion	d[HCl]/dt Moles $l^{-1}s^{-1}g^{-1}$ x 10^7	Net Activity cps Undegraded	Net Activity cps Degraded	Kinetic Chain Length	Number of Radicals per Chain
Low Conversion :						
Bz_2O_2						
0.01	4.3	0.66	0.22	0.020	2640	0.41
0.10	7	0.70	0.70	0.140	823	0.88
AIBN						
0.01	4.0	0.63	0.22	0.022	3103	0.29
0.10	10.9	0.98	0.71	0.014	972	0.89
High Conversion :						
Bz_2O_2						
0.01	80.8	0.88	0.31	0.011	1937	0.59
0.10	72.0	0.99	1.14	0.069	510	1.93
AIBN						
0.01	78.0	0.53	0.19	0.020	3546	0.37
0.10	78.9	1.11	0.46	0.032	1508	0.67

Bz_2O_2 initiated polymers possess more radicals for chain that their AIBN counterparts.

Table 4.20 shows the effect of temperature of polymerisation. The KCL decreases with increase in temperature due to increase in the rate of initiation and consequently in the rate of termination.

The activity increases per gr. of polymer; this increase in end groups with increase in temperature might explain the instability at higher temperatures.

Table 4.20. Effect of Temperature on Thermal Stability of PVC using 0.01 C^{14} labelled Bz_2O_2.

Temperature °C.	Polymer % Conversion	d[HCl]/dt Moles $l^{-1}s^{-1}g^{-1}$	Net Activity cps Undegraded	Net Activity cps Degraded	Kinetic Chain Length	Number of Radicals per Chain
Low Conversion :						
25	4.2	0.30	0.07	0.020	8069	
40	6.7	0.42	0.11	0.025	5008	
60	4.3	0.66	0.22	0.020	2640	0.41
80	18.0	1.13	0.39	0.044	1489	0.32
High Conversion :						
25	80.0	0.13	0.02	0.021	29050	0.1
40	84.0	0.47	0.05	0.025	10563	0.21
60	80.8	0.88	0.10	0.011	5585	0.21
80	78.0	2.08	0.18	0.017	3246	0.15

Table 4.21 shows the effect of conversion on the activity of the polymer. The KCL increases with conversion : this would be due to the decrease in the rate of termination as reaction proceeds and hence also decreasing the number of radicals per chain. Also traces of impurities give a decrease in the KCL. This accounts for the low stability at earlier stages and for the parallel increase in KCL and thermal stability of the polymer at medium conversions.

Table 4.21. Effect of Conversion on Thermal Stability of PVC using 0.01 C^{14} labelled Bz_2O_2 at 60°C.

% Polymer Conversion	Net Activity cps Undegraded	Net Activity cps Degraded	$d[HCl]/dt$ Moles $l^{-1}s^{-1}g^{-1}$ x 10^7	KCL	Number of Radicals per Chain
4.3	0.22	0.020	0.66	2641	0.41
25.0	0.14	—	0.43	3979	
37.8	0.17	—	0.38	3438	
65.5	0.11	—	0.63	5330	
80.8	0.10	—	0.88	5587	0.21

FILM DEGRADATION :

In order to investigate the formation of polyene chains during the degradation of PVC, films were used rather than polymer solutions. The advantages of using films are that chemical interactions with solvent are avoided especially at high temperatures, as is absorption by the solvent in the Visible and UV spectrum.

Films were cast from THF and dried under vacuum for 72 hours before use. The thickness (0.0018") and weight (0.0340 g) were kept constant. The film was cut to a 2.5 x 0.5" size and secured in a teflon frame of the same size. The same degradation reaction vessel and instrumentation were used. The PVC used as a base for this study was emulsion polymer (page 126).

Degradations were run at 65, 80, 100, 120, 135, 153, 198, 250 and 300°C.

Figures 4.30 to 4.37 show partial UV/Visible spectrum obtained for the above temperatures.

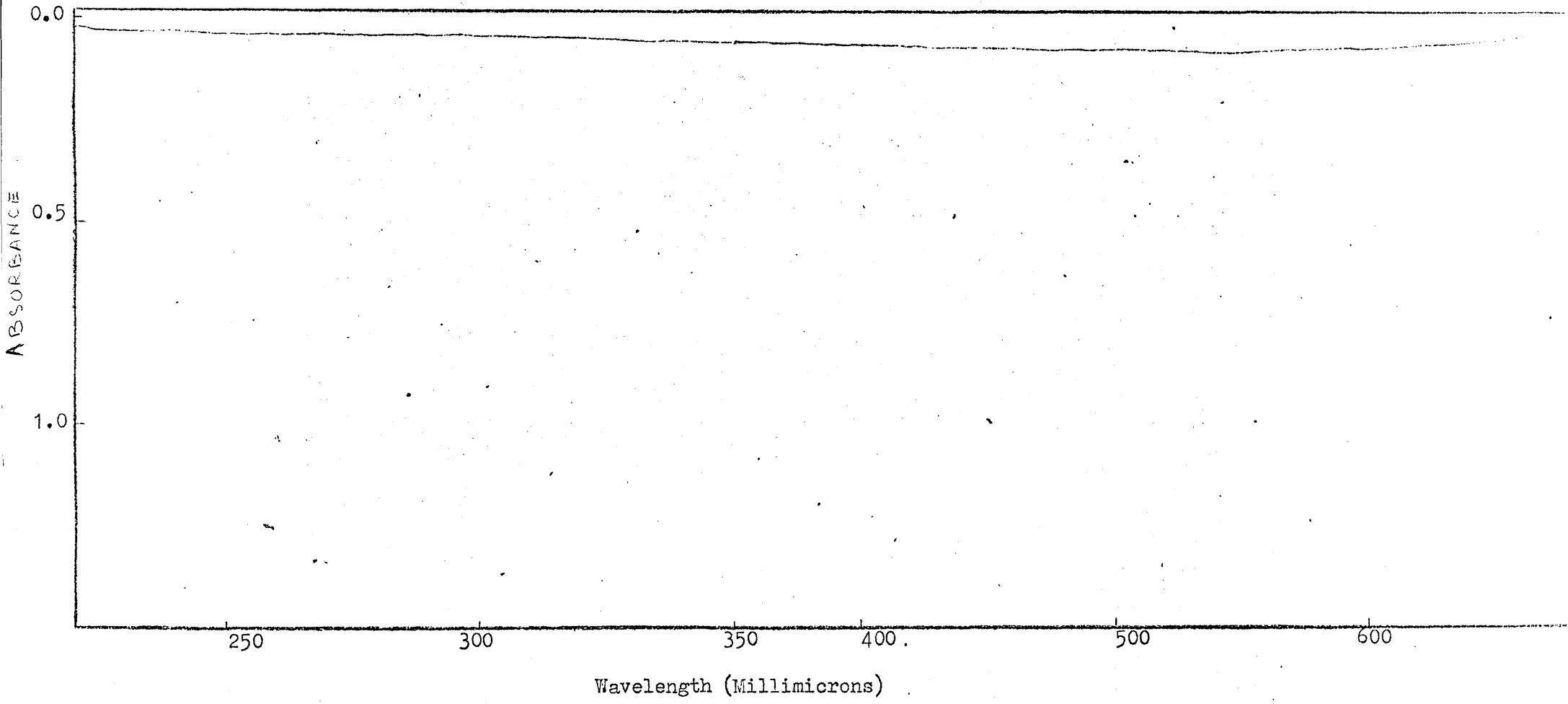


Fig. 4-30 ABSORPTION SPECTRA OF PVC DEGRADED AT 60°C FOR 4760 hrs.

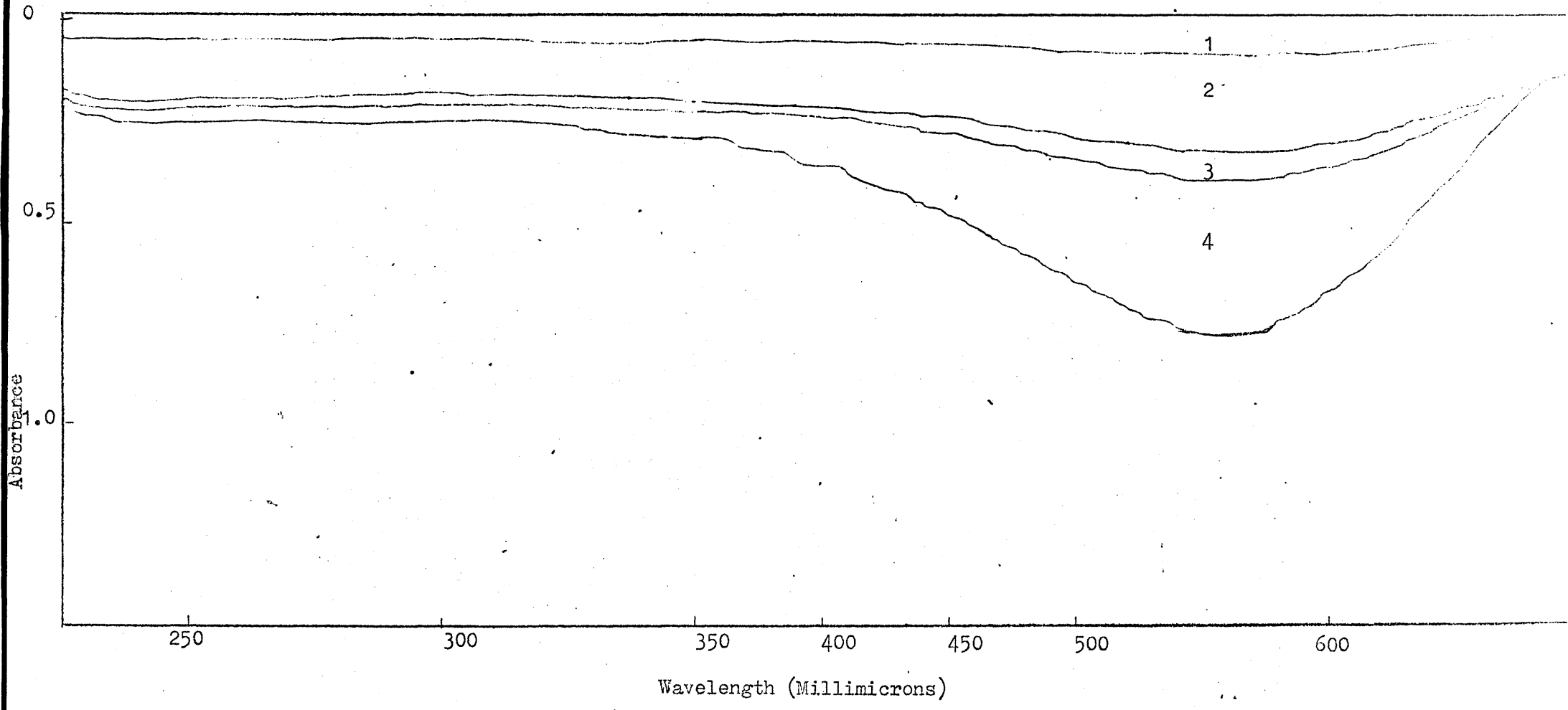


Fig. 4-31 ABSORPTION SPECTRA OF PVC DEGRADED AT 80°C for
1 - 173 hrs
2- 650 hrs
3 - 650 hrs
4 - 2240 hrs

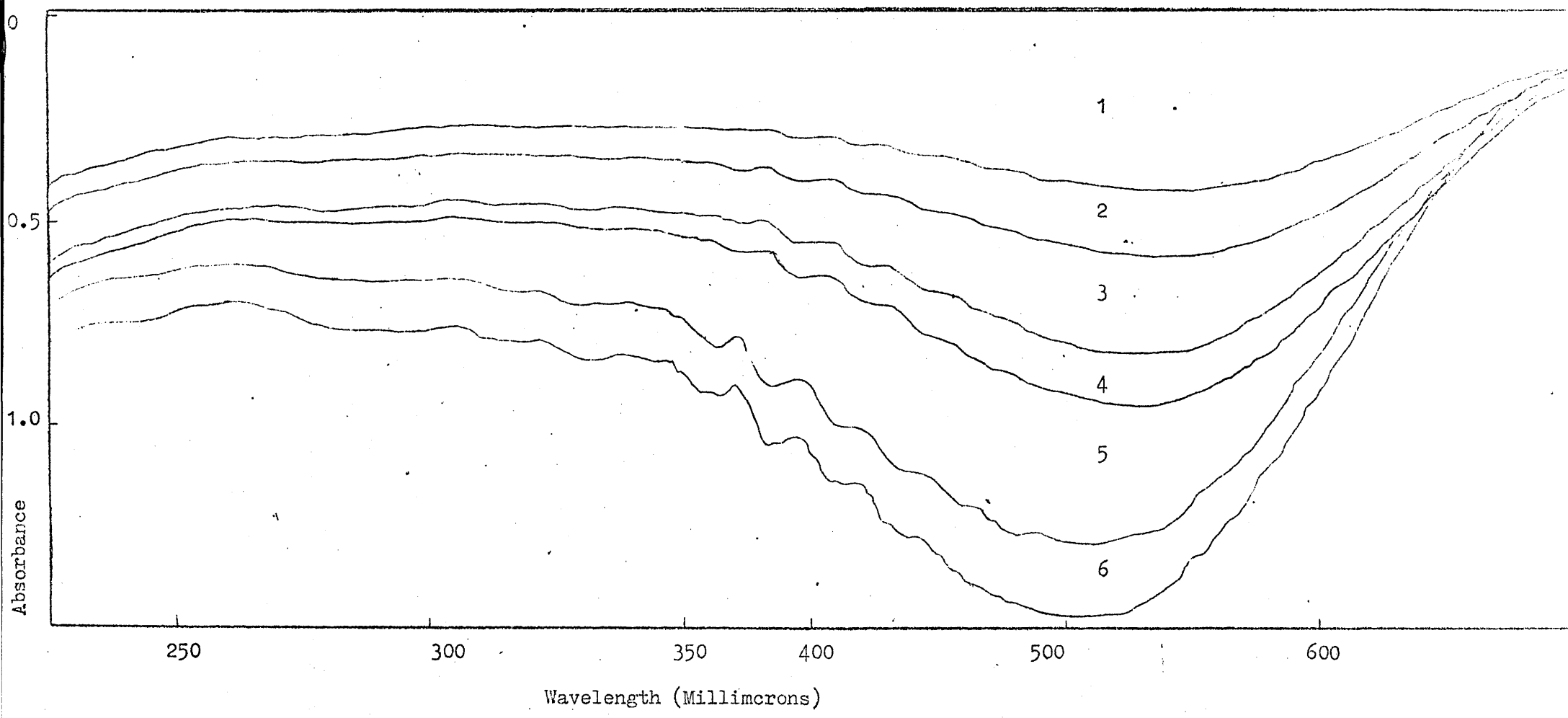


Fig. 4-32 ABSORPTION SECTRA OF PVC DEGRADED AT 100°C For

1 - 263 2 - 350 3 - 560
4 - 685 5 - 920 6 - 1160 hrs.

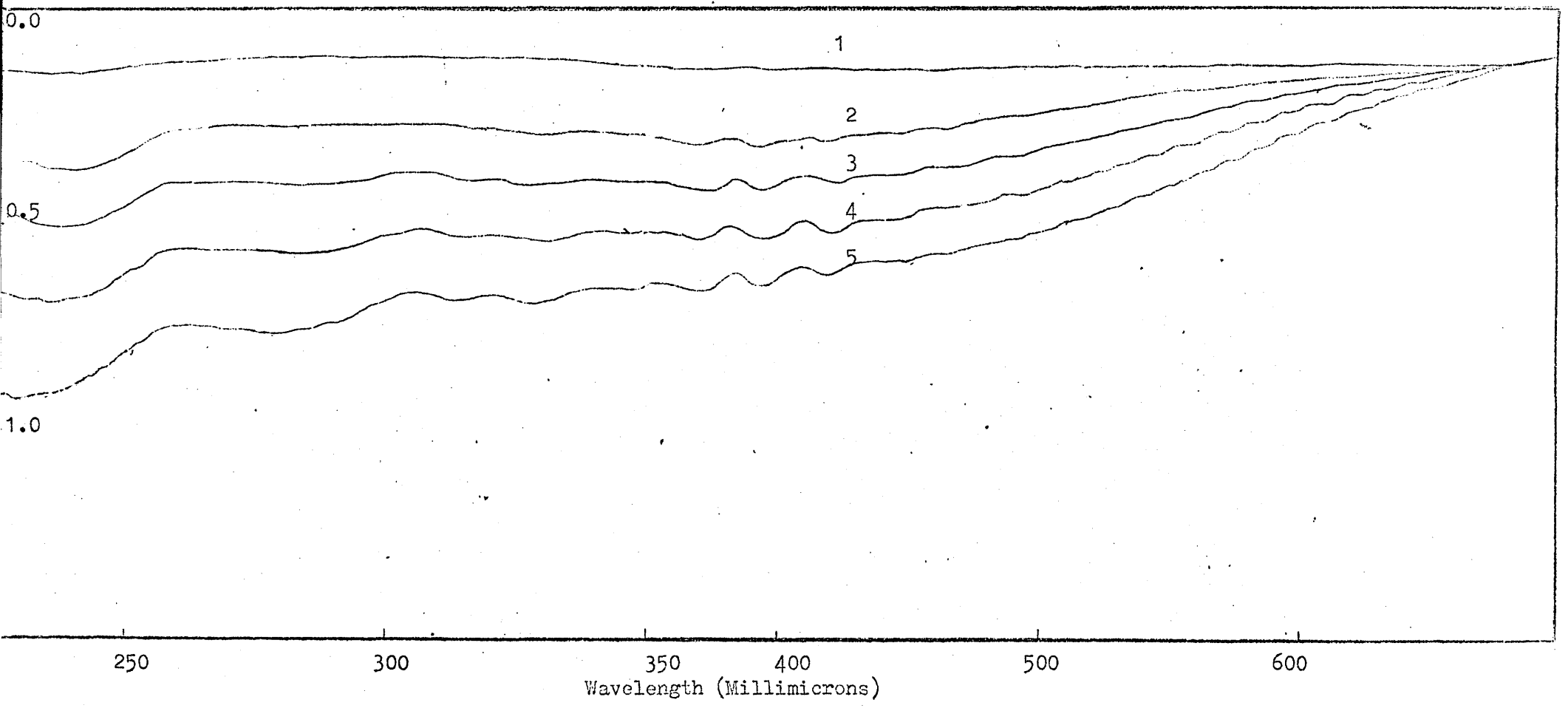


FIG. 4_ 33 ABSORPTION SPECTRA OF PVC DEGRADED AT 120°C for 1 - Initial 2 - 4, 3 - 8, 4 - 25, 5 - 54 hrs.

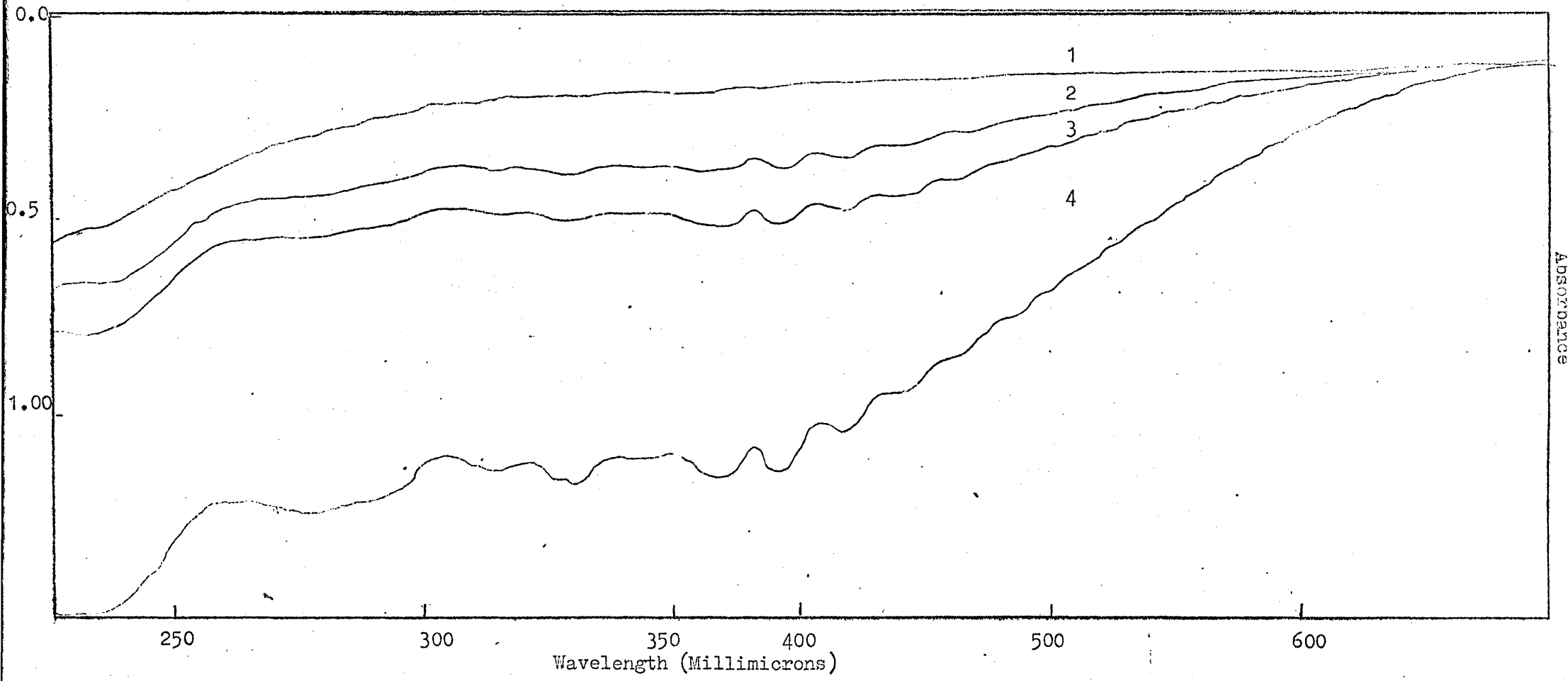


Fig. 4-34 - ABSORPTION SPECTRA OF PVC DEGRADED AT 135°C for
1 - 15 mins 2 - 2 hrs
3 - 4 hrs 4 - 20 hrs

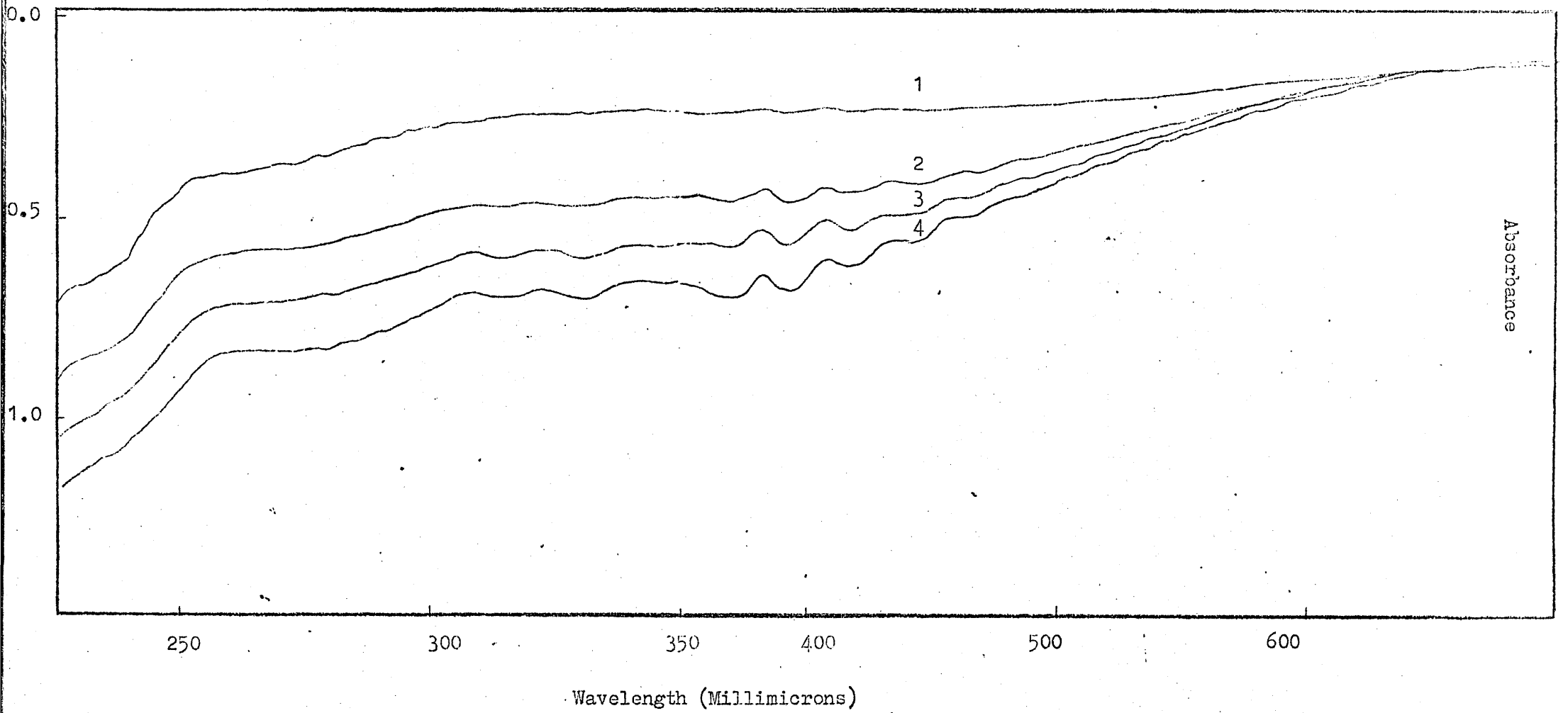


Fig. 4-35 ABSORPTION SPECTRA OF PVC DEGRADED AT 150°C for

1 - 1 hr 2 - 4 hrs
2 - 6 hrs 4 - 9 hrs.

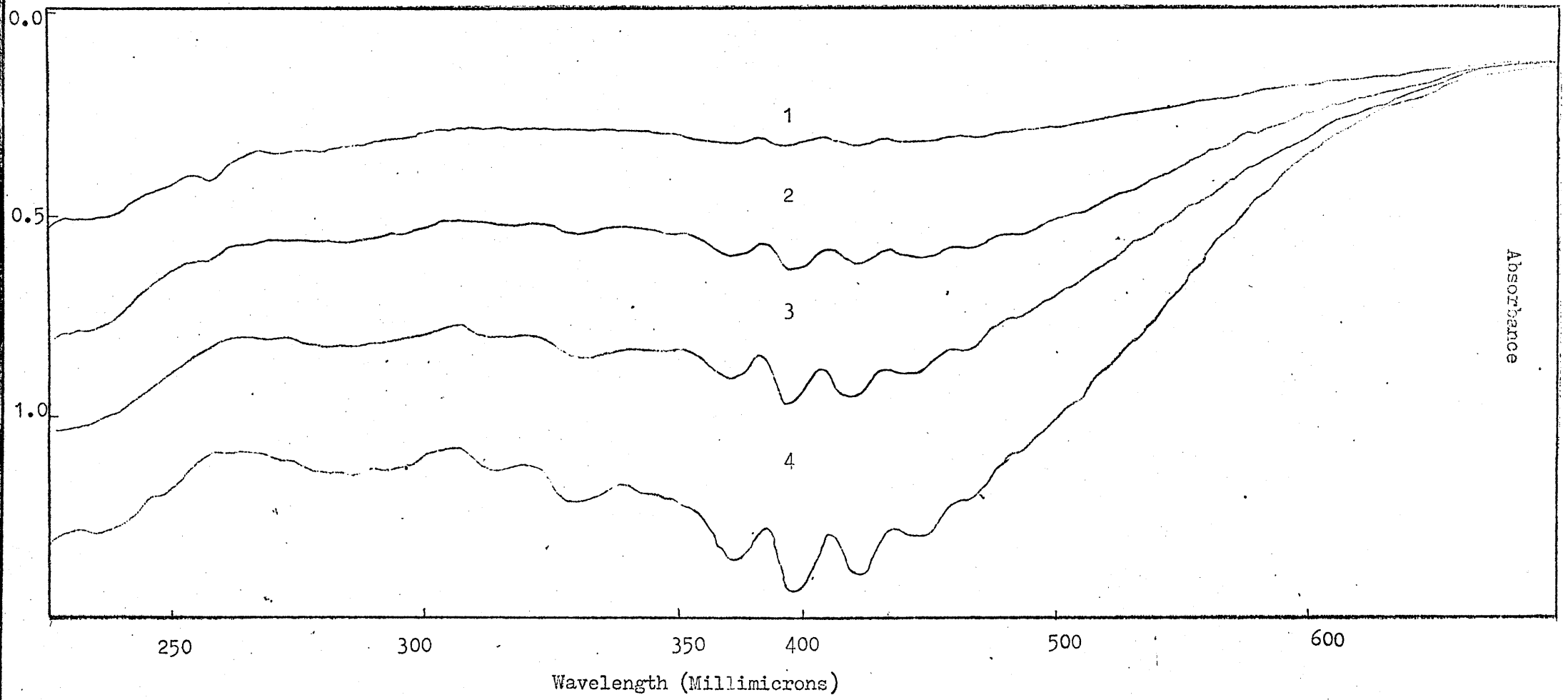


Fig. 4-36 ABSORPTION SPECTRA OF PVC DEGRADED AT 198°C for

1 - 15 mins 2 - 21 mins.
3 - 27 mins 4 - 33 mins.

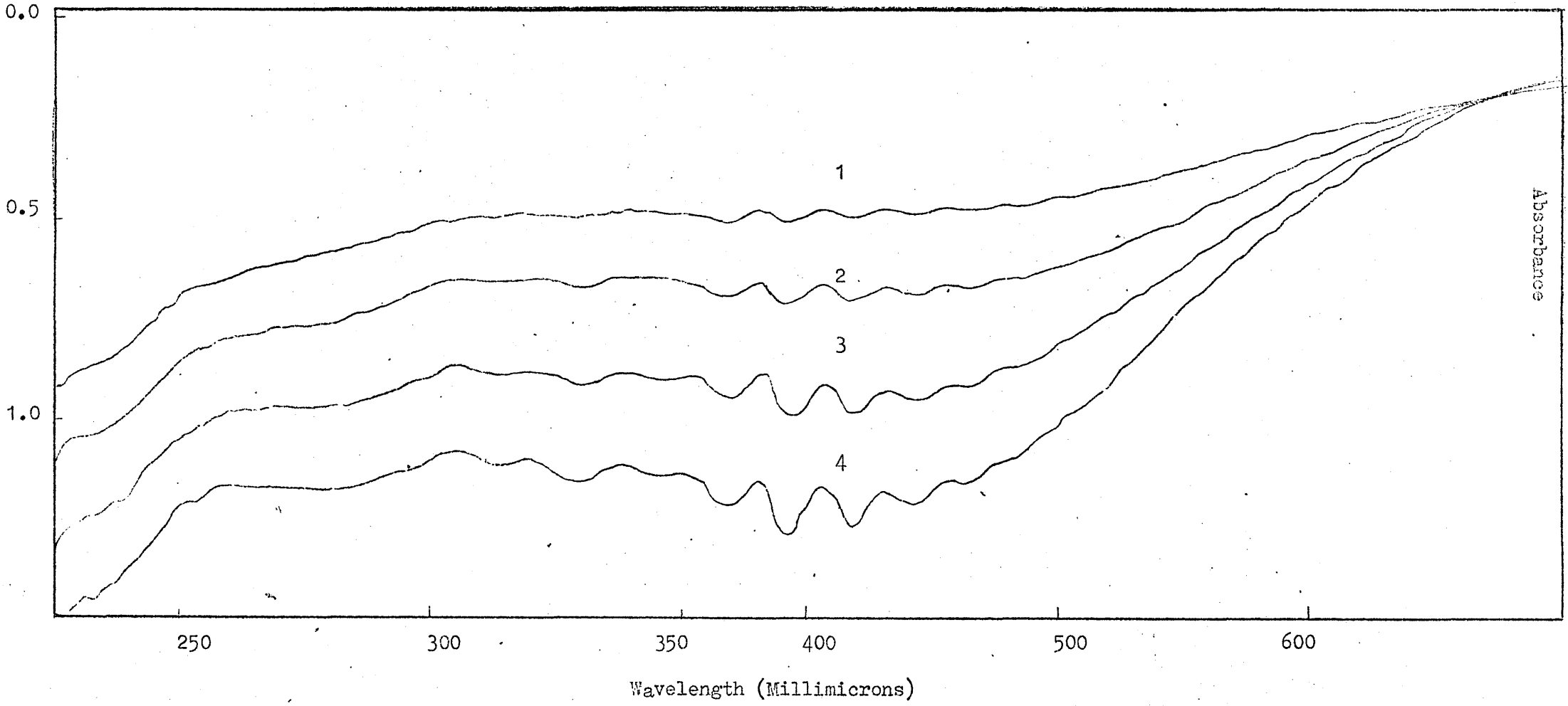


Fig. 4-37 ABSORPTION SPECTRA OF PVC DEGRADED AT 250°C

1 - 4 mins. 2 - 10 mins.
3 - 16 mins. 4 - 22 mins.

The results show that a series of characteristic absorption bands develop during degradation, with discrete maxima at ($\pm$ 5 mμ to accommodate for shifting); 235, 280, 315, 330, 345, 365, 395, 416, 440, 458, 470, 490, 520, 550, 580, and 640 mμ depending on the degradation temperatures.

Table 4.22 shows the highest absorption for the different degradation temperatures.

Table 4.22. Highest Absorption Values

Degradation Temperature °C.	Highest Absorption (m/μ)	
	UV	Visible
250	235	360
198	235	360
153	235	360
135	235	360
120	235	360
100	235	530
80	235	555

The spectra for the 60°C degradation Fig. 4.30 shows very little absorption over the entire wavelength except for the initiation of a very slight and broad maxima at around 550 mμ after 5000 hours.

The spectra for 80°C degradation Fig. 4.31 shows no absorption peaks up to 300 mμ (2 double bonds) with gradual increase to a maximum at 550 (appearing after 400 hours) a band which could be characteristic of about 20 double bonds. The spectra for 100°C. Fig. 4.32 shows the same pattern as in the 80°C degradation spectra with more discrete peaks appearing in the region of 350 mμ culminating in a broad maxima at around 525 mμ instead of 550 mμ after about 70 hours.

A complete transition occurs in the 120°C degradation spectrum Fig. 4.33, with the disappearance of the 550 maxima. The main discrete peaks being at 235, 280, 315, 330, 370, 392, 420, 450, 470 and 490 m

The 135°C and 150°C degradation spectrum Fig. 4.34 and Fig. 4.35 show more distinct peaks at the lower end of the spectrum with the maxima occurring around 230 - 260 mμ , with the high concentration of 2 and 3 double bonds falling off.

The spectrum for the 198°C degradation Fig. 4.36 shows distinct peaks at 235 mμ 280, 315, 330, 345, 370, 394, 420, 445 and 465, with lesser peaks up to 600 mμ . In the 250°C degradation spectrum Fig. 4.37 the most prominent peaks are at the lower end of the spectrum with the maxima at 235 mμ and prominent broad peak at 280 mμ . In the visible region the peaks are less distinct and tend to taper off at about 400 mμ as opposed to 450 mμ in the earlier case.

At 300°C, the peaks become much less discrete and due to the speed of the degradation reaction only few scans were obtained. The inaccuracy of these runs are also significant due to the short exposure periods and high temperature disparity.

These results show two new findings;

(a) A new low temperature at which polyene chains could be formed in PVC, at around 80°C.

(b) The existence of 2 different mechanisms for the conjugated double bond formation. The first occurring at low temperature degradation, which results in the formation of long sequence double bonds, about 20 or more (as indicated by the maxima formed at 530 to 550 mμ).

The second mechanism occurring at 120°C and higher, reflecting a series of absorption maxima which diminishes in intensity as the wave length increases beyond 390 mμ .

Fig. 4.38 shows the effect of degradation time on the 520 mμ absorption band for low temperatures, while Fig. 4.39 shows the same relation for higher temperatures, 200, 250 and 300°C.

Fig. 4.40 shows the relation of degradation time on the 365 mμ absorption band for low temperatures (80, 100, 120, 135 and 150°C) while Fig. 4.41 shows the same relation for the higher temperatures of degradation (200, 250 and 300°C).

The results show that two completely different types of spectrum are obtained when films of PVC are degraded thermally, depending on the degradation temperature. At 120°C and above one type of spectrum is obtained, while at 100°C and below a second type of spectrum is obtained. The rates of degradation as measured by the change in absorbance, differ enormously for the two temperature ranges, which also indicates a difference in the mechanism of the degradation for the two types. Of interest too, is the fact that the high temperature degradations give similar spectrum to those obtained in solution degradation with esters and chlorinated hydrocarbons. The spectrum obtained at low temperatures show a similarity to those obtained in solution degradation in presence of amides, specifically dimethyl formamide.

A comparison of polymers prepared by different processes was also performed by degrading their films at 198°C. Fig. 4.42 shows the spectrum of commercially prepared suspension PVC as described in Chapter 2. The stability of this film was markedly less than that made of emulsion PVC, Fig. 4-36. The maxima occurs at around 360 mμ . The location of the other discrete peaks are the same as in emulsion except that they seem to be weaker and the tapering off occurs earlier, around 400 mμ as opposed to 450 mμ in case of emulsion polymers.

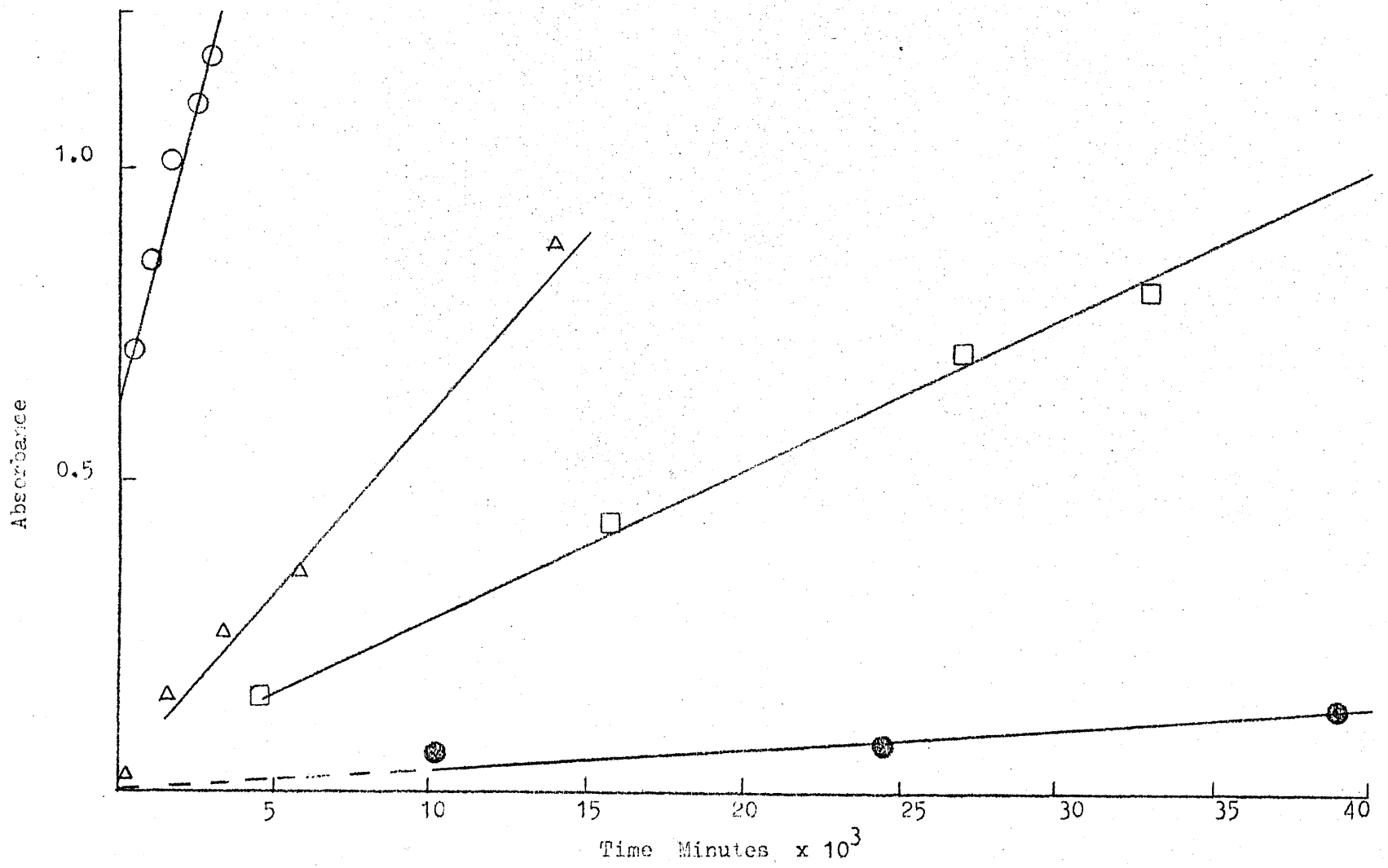


Fig. 4-38 EFFECT OF DEGRADATION TIME ON THE ABSORBANCE AT 520 mμ FOR LOW DEGRADATION TEMPERATURE

80°C ●
100°C □
120°C △
135°C ○

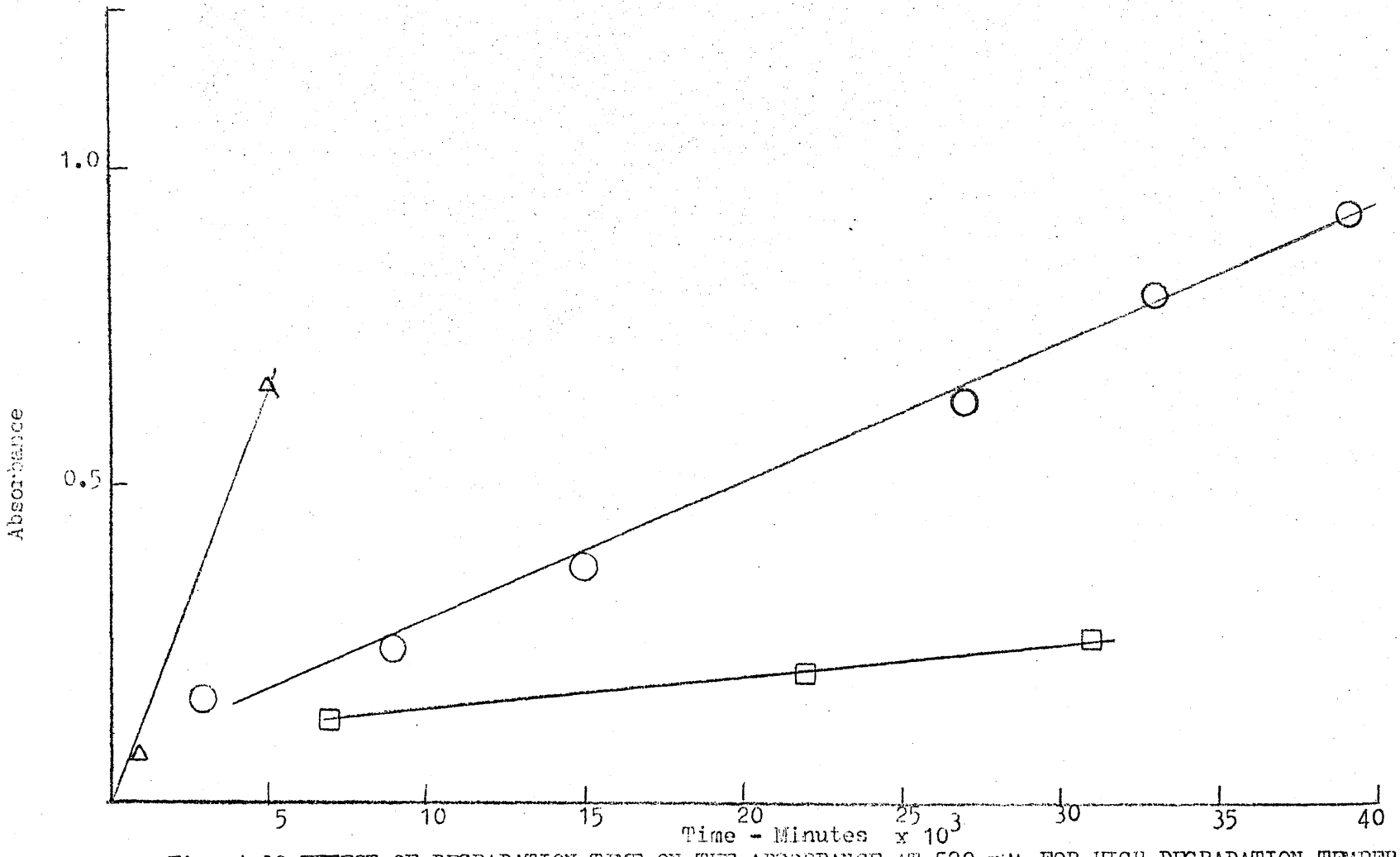


Fig. 4-39 EFFECT OF DEGRADATION TIME ON THE ABSORBANCE AT 520 mμ FOR HIGH DEGRADATION TEMPERATURES

200°C —□— 250°C —○— 300°C —△—

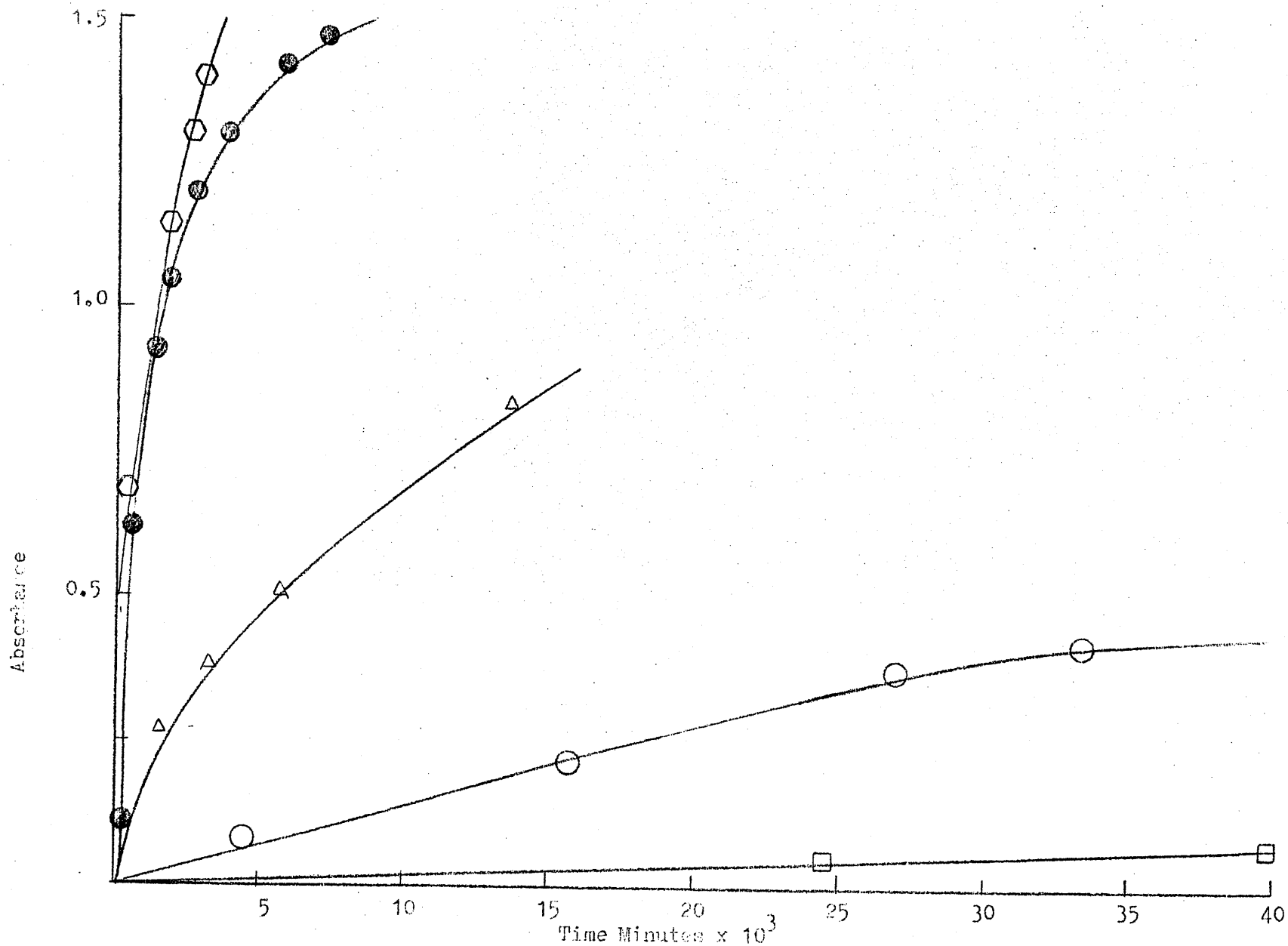


Fig. 4-40 EFFECT OF DEGRADATION TIME ON THE ABSORPTION AT 365 mμ FOR LOW DEGRADATION TEMPERATURES

80°C — 100°C — 120°C — 135°C — 150°C —

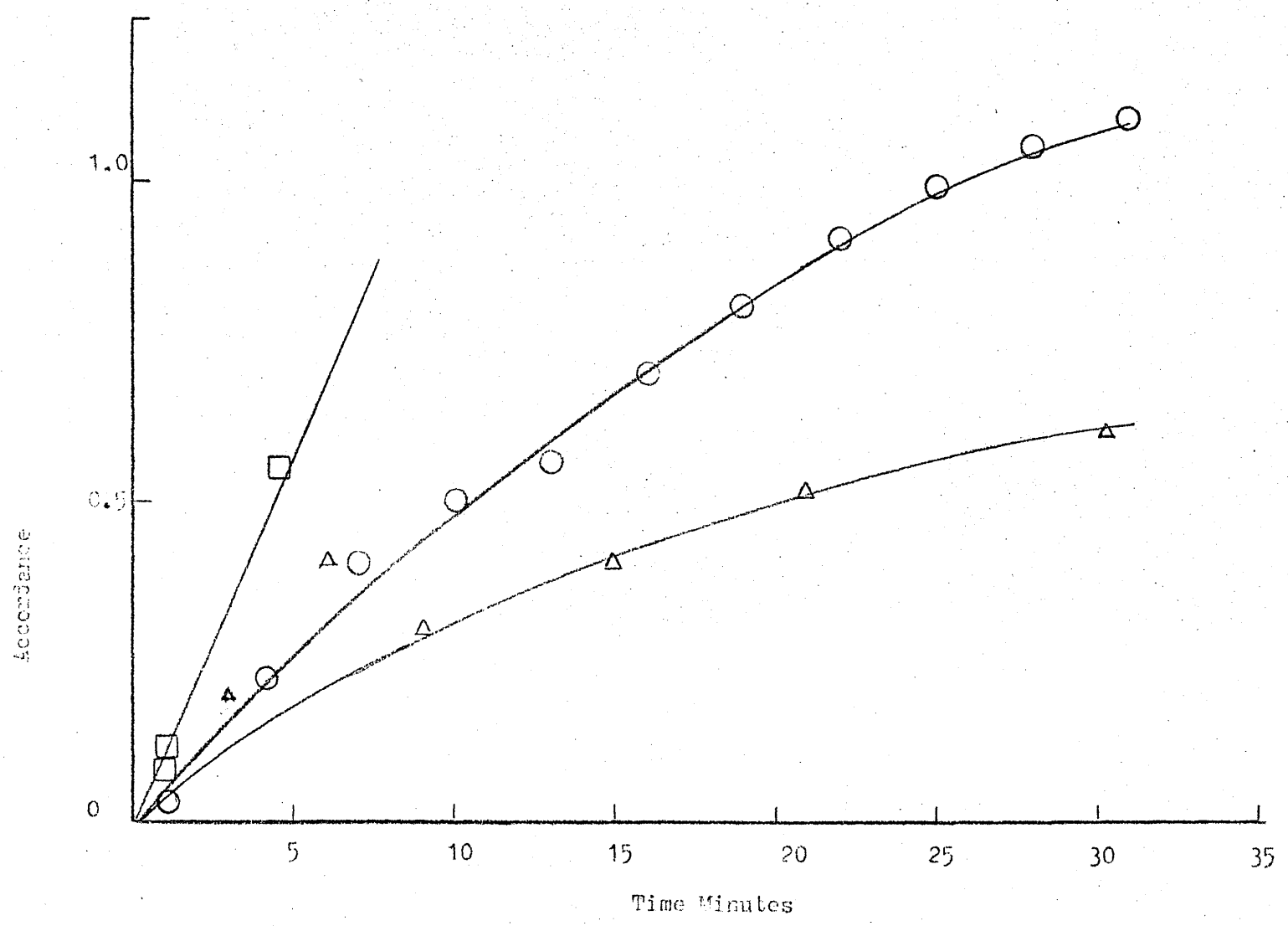


Fig. 4-41 EFFECT OF DEGRADATION TIME OF THE ABSORBANCE AT 365 mμ for HIGH DEGRADATION TEMPERATURES

200°C —△—
250°C —○—
300°C —□—

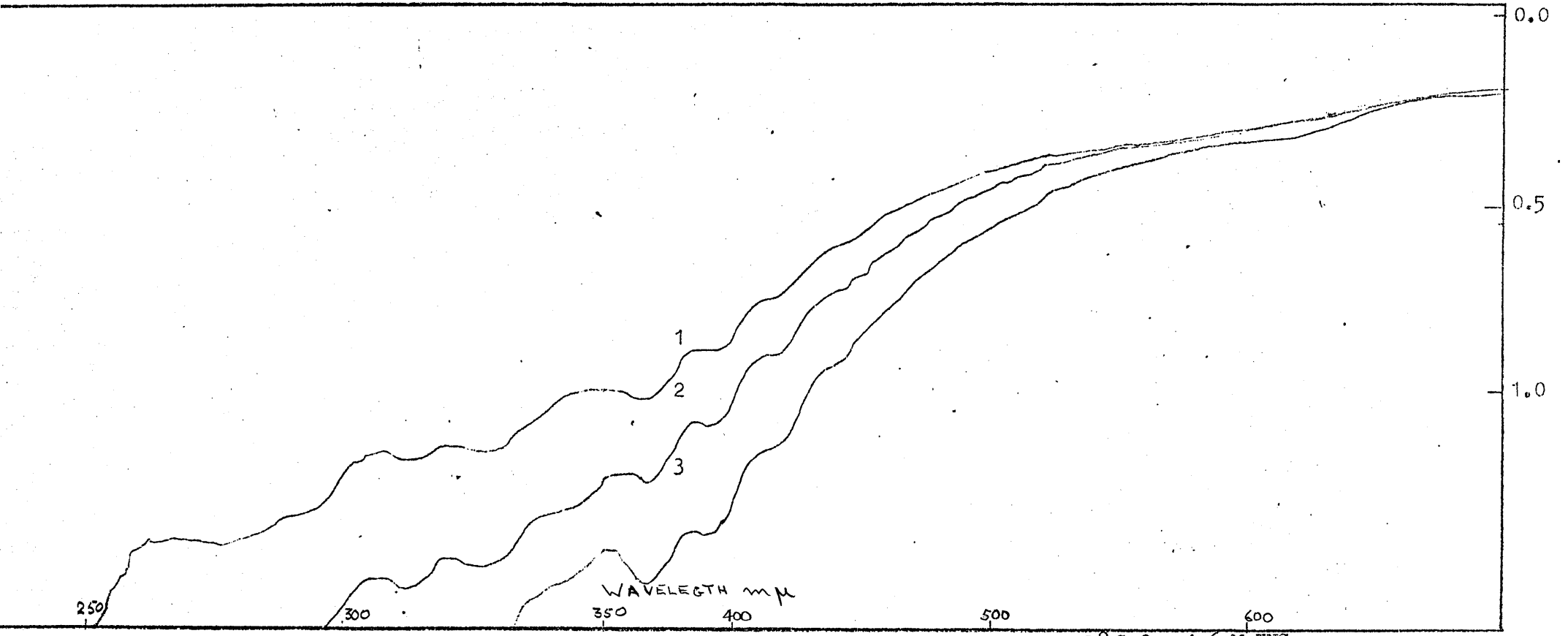


Fig. 4-42 ABSORPTION SPECTRA OF SUSPENSION PVC DEGRADED at 198°C for 1-6 M INS
2-12 MINS. 3-18 MINS.

Fig. 4-43 shows the spectrum for a laboratory bulk prepared polymer at 60°C using 0.01 M% Bz_2O_2 taken to 96% conversion. The stability of this polymer is less than that of the emulsion polymer but similar to that of suspension polymer.

Fig. 4-44 is a spectrum for a solution prepared PVC in DMF. This particular solution polymer was much less stable than PVC polymerised in the presence of other solvents. It was degraded at 138°C instead of 198°C because of its instability. The spectrum shows a new maxima in the UV region at 255 m μ . The remainder of the peaks are similar to those obtained with bulk prepared PVC films. Table 4.23 shows a comparison of the stability of emulsion, suspension and bulk polymers, previously discussed, in terms of their absorption at the 360 m μ band after a constant period of time at 198°C.

Table 4.23. Absorption of Differently Prepared PVC After Degradation at 198°C.

Polymer	Absorbance at 360 m μ after 30 Minutes Degradation at 198°C.
Commercial Emulsion	0.70
Commercial Suspension	1.20
Laboratory Bulk	1.37

Fig. 4-45 shows the effect of conversion in the Visible absorption spectrum. The three polymers were all polymerised at 60°C using 0.01 M% Bz_2O_2 to 60, 80 and 96% conversion. There is a decline of stability with increase in conversion.

Fig. 4-46 shows the effect of polymerisation temperature on the stability of the polymer as observed in the Visible absorption spectrum. The polymer is one prepared at - 50°C by photoinitiation of AIBN (0.01 M%)

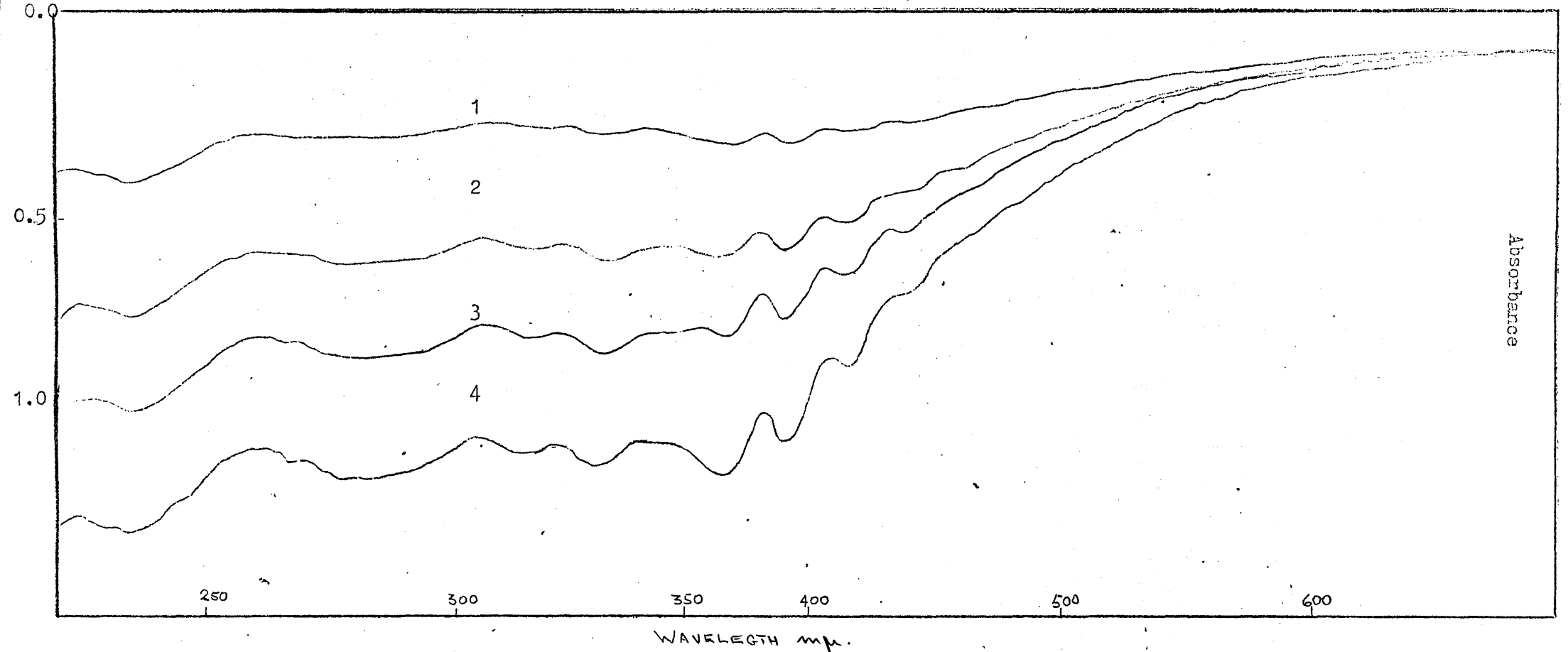


Fig. 4-43 ABSORPTION SPECTRA OF BULK LAB PREPARED PVC DEGRADED AT 198°C for
1 - 6 MINS 2 - 12 MINS
3 - 18 MINS 4 - 24 MINS

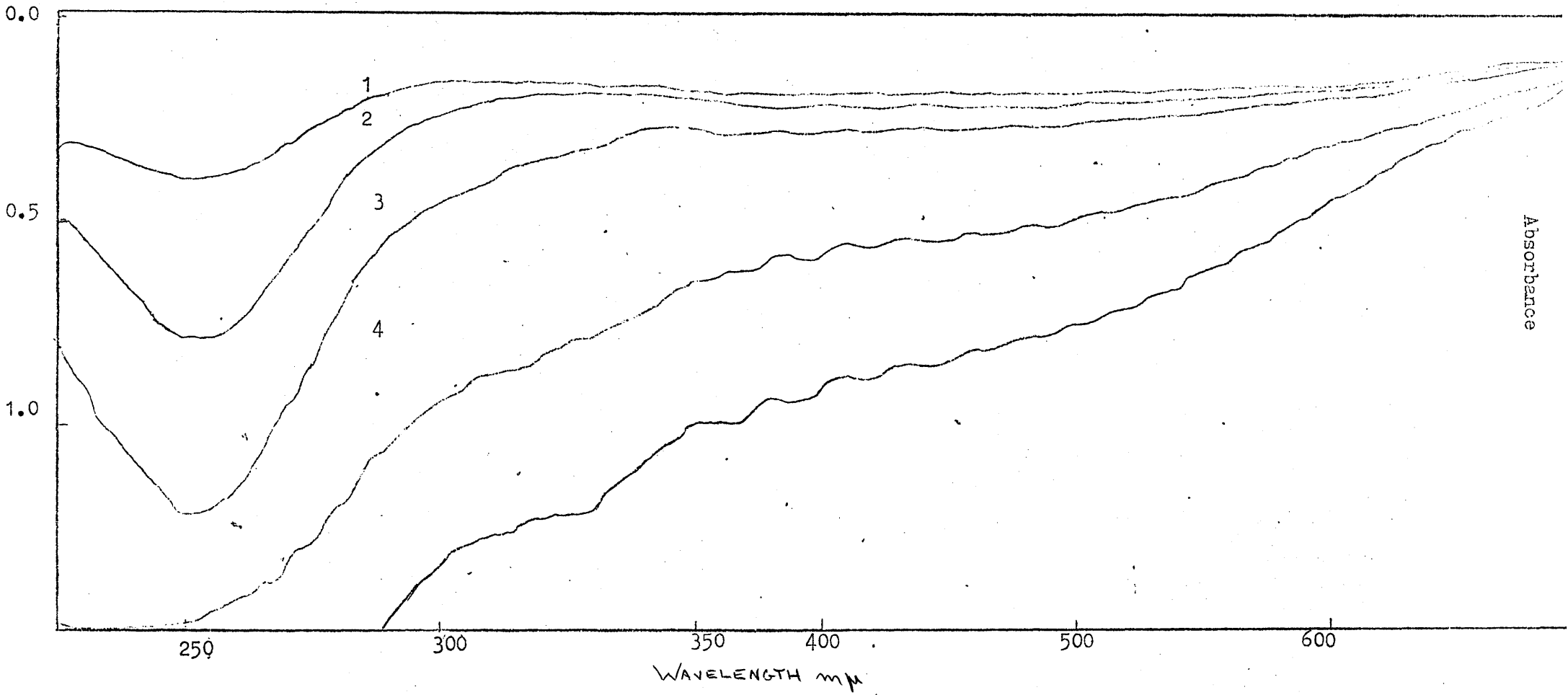


Fig . 4-44 ABSORPTION SPECTRA OF SOLUTION. PVC PREPARED IN PRESENCE OF F

1 - 170 MINS 2 - 6 HRS.
3 - 14 HRS. 4 - 51 HRS.

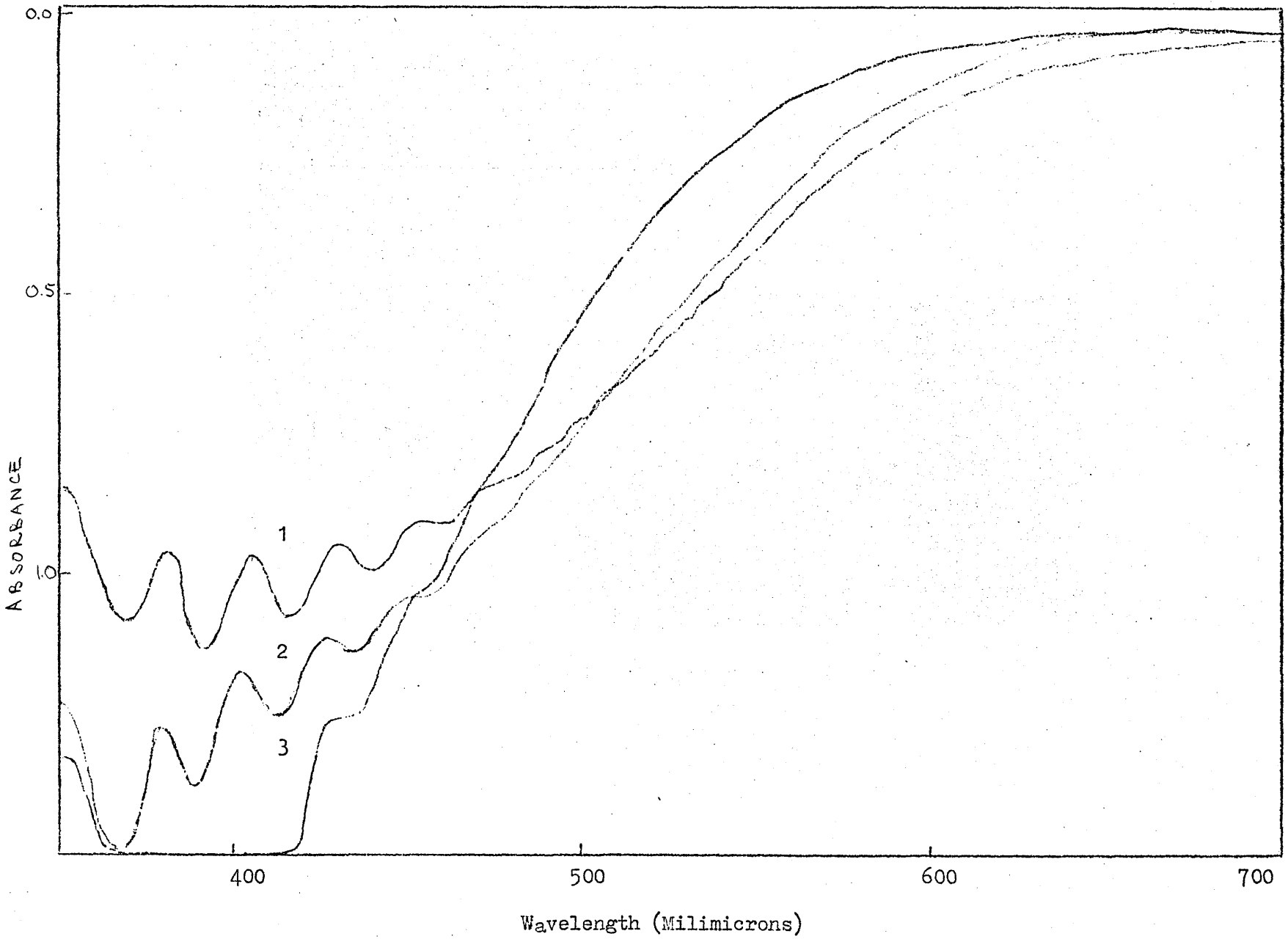


Fig. 4-45 ABSORPTION SPECTRA OF PVC PREPARED AT 60°C TO DIFFERENT POLYMER % CONVERSION

1 - 65%
2 - 81%
3 - 96%

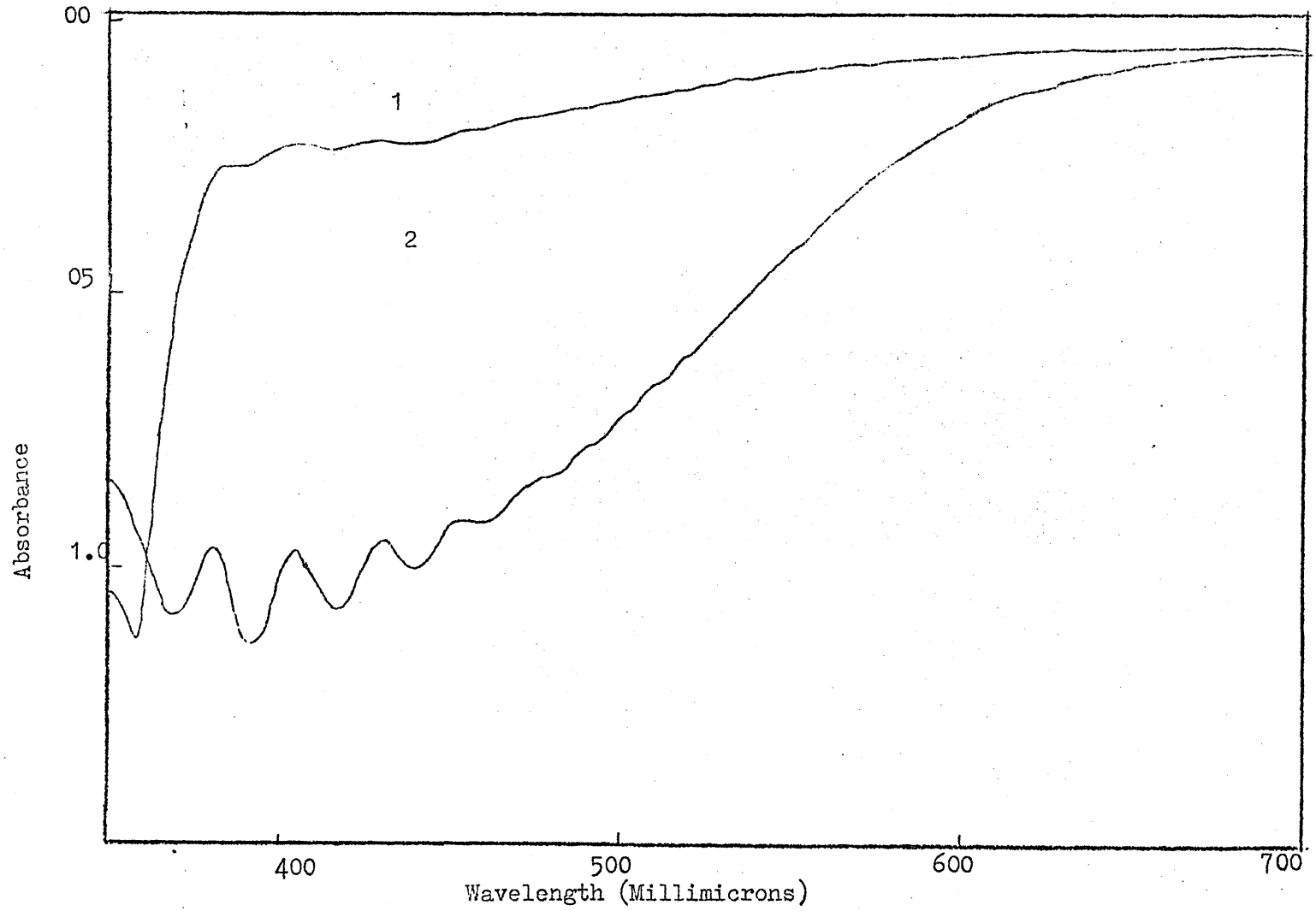


Fig. 4-46 ABSORPTION SPECTRA OF
1 - PVC prepared at - 50°C
2 - PVC prepared at 60°C

Of interest is the fast rate of double bond formation in the first 10 minutes followed by a very slow increase in the absorbance at 360 m wavelength.

Comparison of Stability of Differently prepared PVC

The activation energies for different polymers were obtained by plotting the logarithm of the rates of dehydrochlorination against the reciprocal of absolute temperatures of degradation. Table 4.24 shows the results obtained.

Table 4.24 Activation energies for degradation for differently prepared PVC

Polymer	Intrinsic Viscosity	Polymer % Conversion	Initiator and Concentration	Polymerisation Temperature °C	E k cal/mole
Commercial Emulsion (PEVIKON JLB-51)	0.9	-	lauroyl peroxide	40	30
Commercial Suspension (GEON III)	0.8	-	lauroyl peroxide	40	21
Laboratory Bulk	0.80	37.8	BZ_2O_2-0.01	60	25
	0.99	96.0	Bz_2O_2-0.01	60	23
Laboratory Photo.	1.08	20.0	AIBN 0.01	50	36

The above activation energies were obtained from solution degradation at 187, 198, 212 and 243°C.

The activation energy for commercial emulsion was also calculated from dehydrochlorination rates of PVC film at 100, 120, 135, 153, 198, 250 and 300°C. Fig. 4-47.

The value obtained was 22 k cal/mole. The activation energy of polyene formation obtained from optical density rates was also calculated

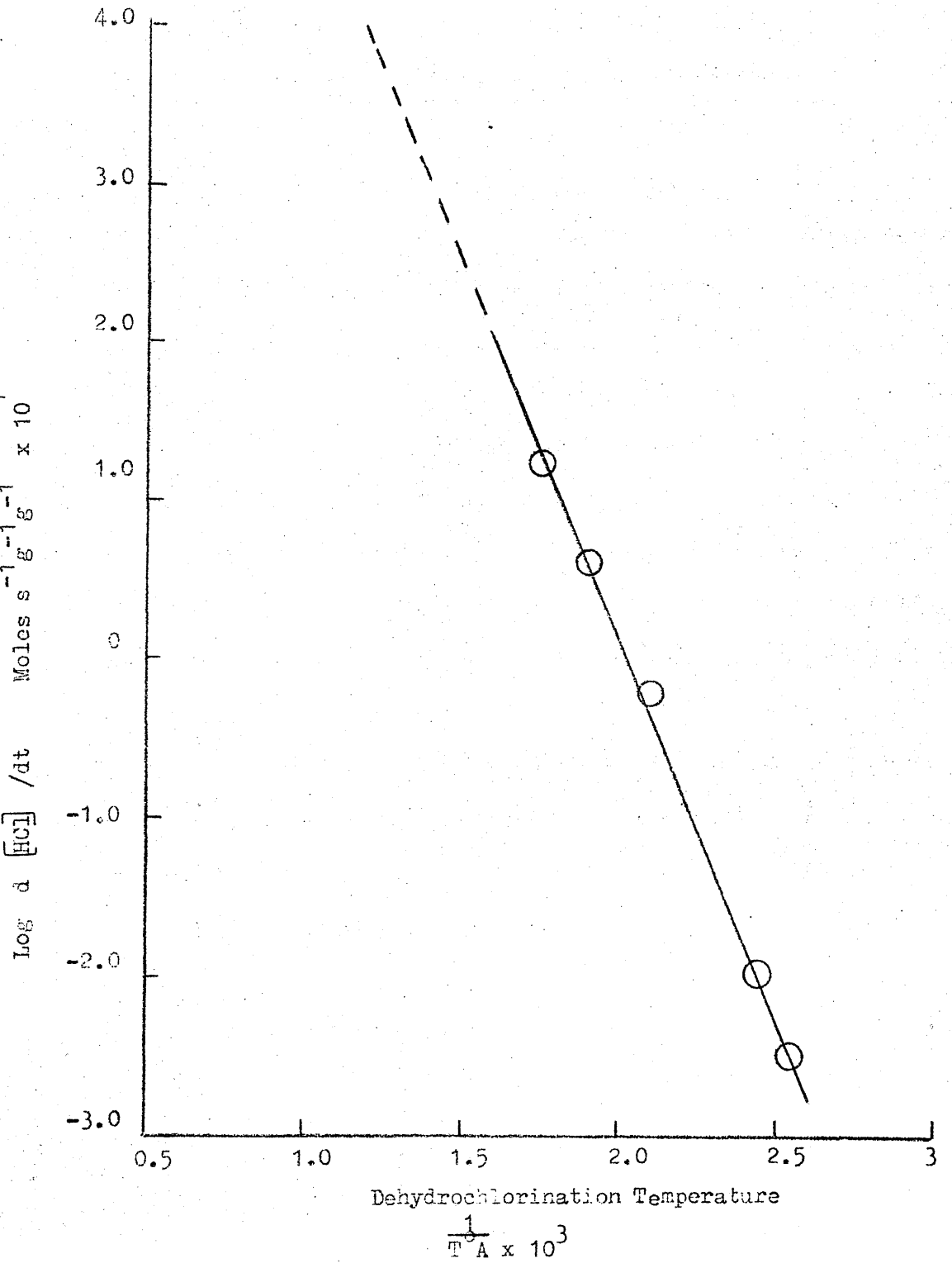


Fig. 4-47 DEHYDROCHLORINATION ACTIVATION ENERGY PLOT FOR PVC FILM

for 520 and 365 mμ wavelength Fig. 4-48 and 4.49 and gave a value of 26 K cal/mole at 520 mμ and 33 K cal/mole at 365 mμ indicating two different reaction mechanisms.

Thus there is a variety of reasons why reported activation energies for the degradation of PVC tend to cover a wide range.

The method of polymerisation, the type and concentration of initiator used, the polymerisation temperature, extent of polymer conversion and method of purification will all have their effect on the E value.

It is also apparent that the form in which the polymer was degraded in, could give rise to different activation energies. In this study the value of film degradation (22 K cal/mole) was much lower than the one obtained from solution degradation (30 K cal/mole). This could be due to (a) the lack of the HCl solubility effect of a solvent and the absence of diffusion barriers. (b) an HCl catalytic effect (c) the fact that in film we are nearing a unimolecular situation (d) the possibility of a stabilising effect by the solvent either through a physical or chemical side reaction.

The activation energy for the polyene formation at high temperatures (365 mμ bond) is higher than the activation energy of dehydrochlorination by about 11 K cal/mole. However, the activation energy for polyene formation at low temperature is greater by only 4 K cal/mole.

DISCUSSION.

The conditions under which vinyl chloride is polymerised have been found to affect both the kinetics of the process and the nature of the polymer formed. Consequently, it was to be expected that the thermal stability of the polymer would also vary as the conditions of the polymerisation were altered. However, the variations in the observed rates of degradation of PVC prepared under varying conditions have, in many cases, been unexpected.

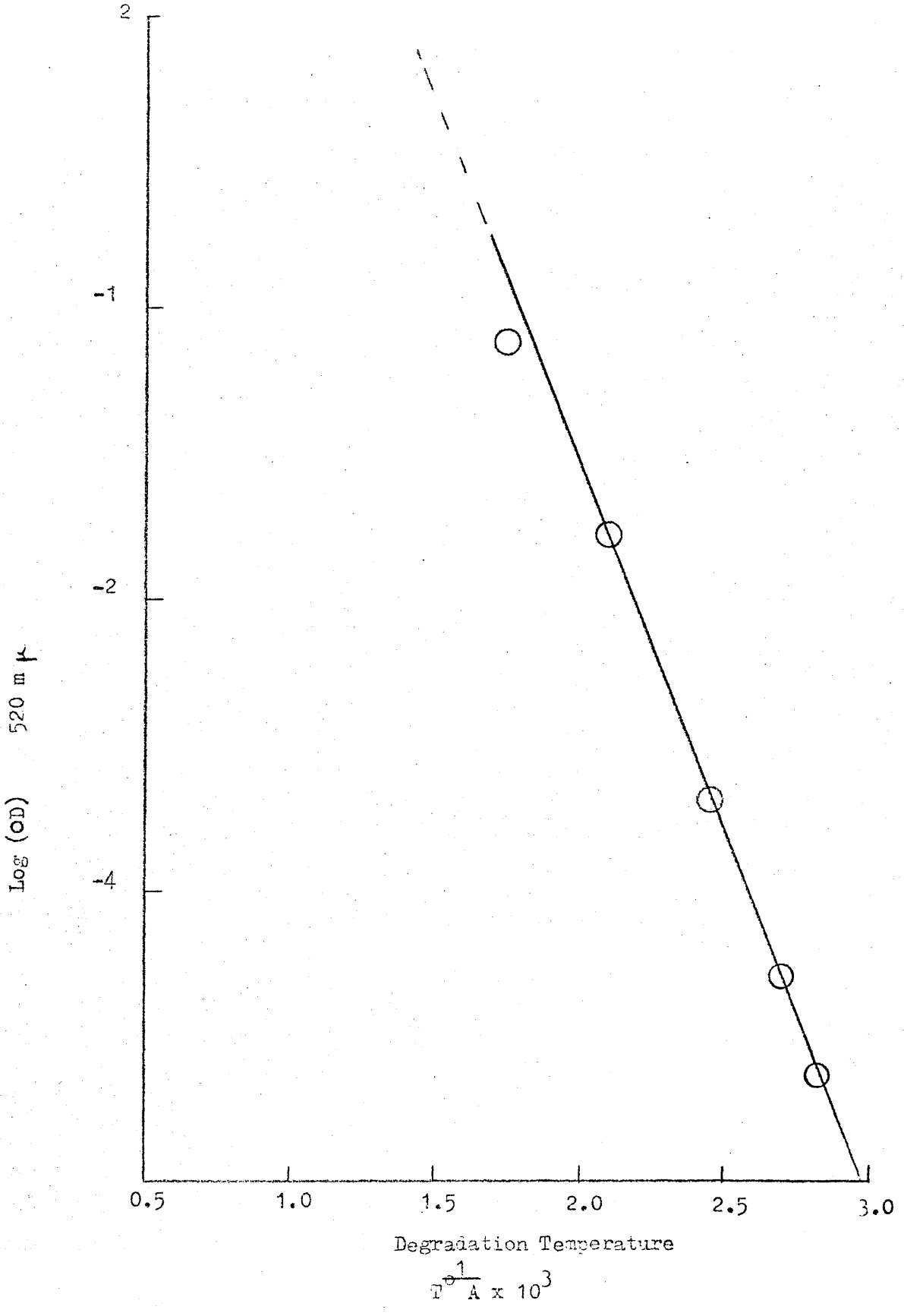


Fig. 4-48 ACTIVATION ENERGY PLOT FROM OPTICAL DENSITY MEASUREMENTS AT 520 mμ Wavelength

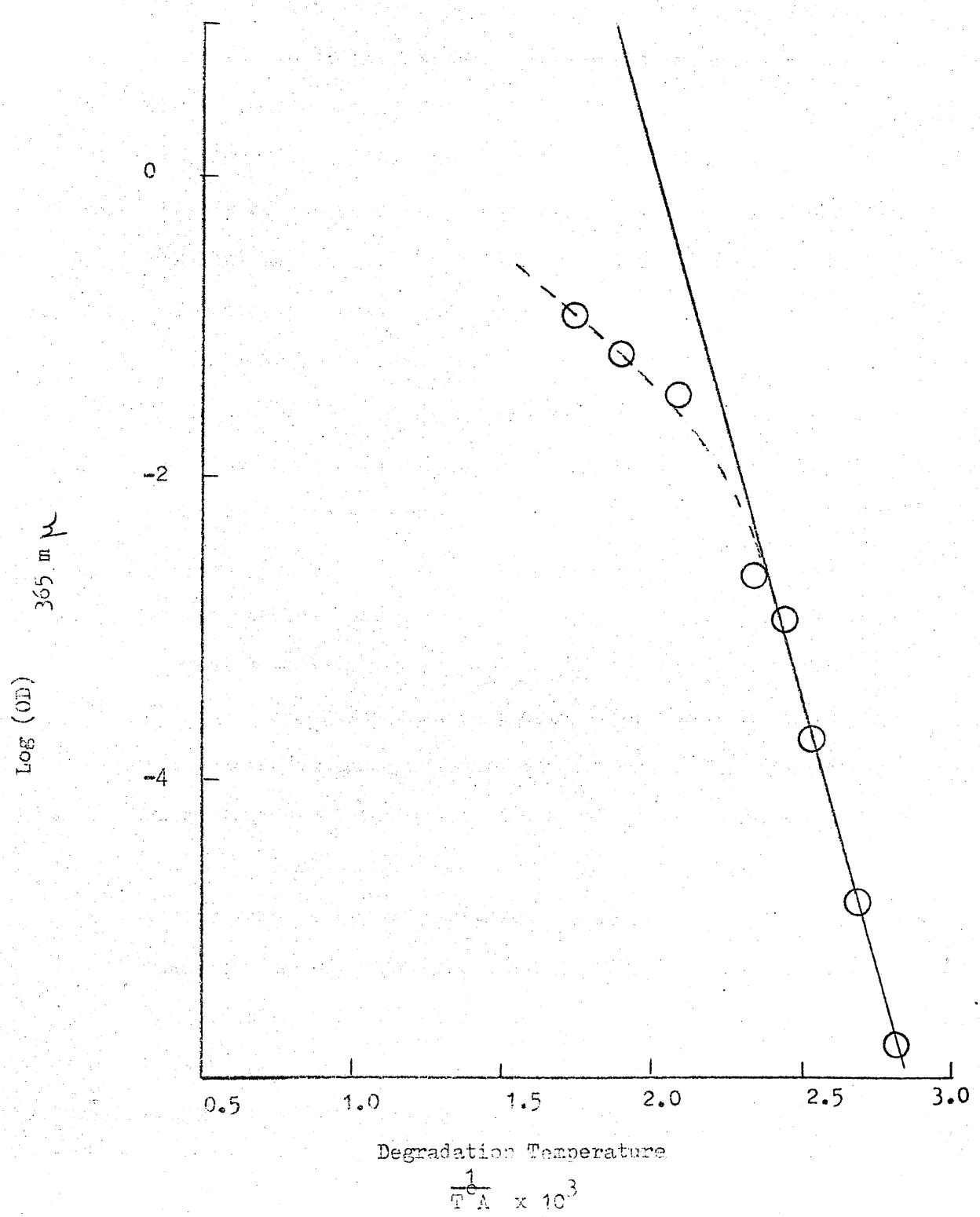


Fig. 4-49 ACTIVATION ENERGY PLOT FROM OPTICAL DENSITY MEASUREMENTS AT 365 m μ WAVELENGTH

For PVC, produced in bulk, it has been found that as the polymerisation temperature is increased the thermal stability of the polymer thus formed is decreased. The changes in the rates of dehydrochlorination of the samples with temperature seem to be uniform as reflected by the straight line relation obtained from the temperature coefficient curves. The molecular weight study of these polymers has shown that an increase in polymerisation temperature also causes a decrease in the molecular weights of the resultant polymers. Thus, it is possible that some parallel may exist between the variations in both properties as the polymerisation temperature increases.

Although the decreases in molecular weight may be accounted for on the basis of the 'occlusion theory' is is more likely that they are the result of an increase in chain transfer to monomer reactions or a decrease in the stereoregularity of the polymer affecting the rates of propagation, chain transfer and termination. These causes may give rise to structural imperfections in the polymer chain which can affect its thermal stability.

As the results have been calculated for a fixed weight of polymer being degraded under standard conditions, it is likely that as the molecular weight decreases, the sample will contain a greater number of smaller polymer chains each with an unstable end group which will cause an increase in the overall rate of dehydrochlorination measured. The results suggest, therefore, that the HCl loss is in some way connected to the concentration of polymer chain ends and that these must be a major contributory factor in determining the thermal stability of PVC. The exact nature and concentration of these chain ends may vary. Initiator fragments may be present to a sufficient extent to affect the rate of degradation. Other likely starting points for dehydrochlorination will be unsaturated groups formed by disproportionation reactions of growing polymer chain ends or by chain transfer to monomer. Several structures

for chain ends formed by monomer chain transfer are possible but the most plausible reaction schemes lead to a chlorine atom at the alpha position relative to the double bond.

$$\sim\sim CH_2 - CHCl - CH = CHCl$$

This structure is unstable and it is apparent that allyl activation will result in HCl loss and that zipper type dehydrochlorination can proceed down the polymer chain. As it is probable that the amount of chain transfer to monomer will increase with increasing polymerisation temperature it is likely that the major causes of unsaturation and the decrease in the thermal stability of PVC prepared at elevated temperatures will be these reactions.

The relation found between the extent of conversion to polymer and the rates of dehydrochlorination is a novel one. A curve is obtained when thermal stability is plotted against conversion with stability having a maxima around 40-50% conversion. A possible explanation may be that as the conversion increases there may be the removal, by reaction, of extraneous impurities from within the system. These impurities, which may be a source of instability, can affect the molecular weight and it is possible that they may undergo a form of copolymerisation with vinyl chloride. One such impurity may be butadiene which may be present in vinyl chloride and which may remain even though a rigorous purification cycle has been undertaken. Such an impurity could cause a decrease in the thermal stability of PVC, prepared at the initial stages of conversion, but as the reaction proceeds, the impurity will be mopped up, and consequently, will have a lesser effect on the thermal stability of PVC. The fact that the stability decreases again towards the end of the reaction, may be due to an increase in the number of branch points due to chain transfer

to polymer. Alternatively, at the later stages there should be a decrease in molecular weight, due to decrease in monomer concentration and consequently the chain end fragments will become more important and the stability will decrease.

One factor that has been ignored in the past is that the thermal degradation itself could be initiated simultaneously or competingly, while the polymer is being formed. Impurities would be the source of such a degradative polymerisation reaction. Its extent depends on the temperature and other reaction variables and could involve free radical reactions. This reaction could have two effects (1) competing with the polymerisation reaction especially at low conversion resulting in either shortening polymer chain formed and (2) creating a new degraded modified species which will further participate in the reaction giving a different polymer.

The above is based on a number of results noticed in this study

(a) Dehydrochlorination (although at a low rate) can take place at temperatures as low as $80^{o}C$.

(b) High temperature polymerisations produce low moleculer weight, degraded polymer as evidenced by the discolouration of polymer, short low inhibition periods, high d [HCl] /dt rates (vertical slope).

(c) Unpurified polymers have short or no inhibition period followed by a retarded rate indicating either the presence of low concentration of adsorbed HCl or very low unstable molecules which are washed away in consequent purifications.

(d) the flattening of both the low temperature/and/high initiator curves of % conversion against d [HCl] /dt. In the former the degradative effect of temp. is eliminated and in the latter the reaction is speeded up amounting to shorter exposures of the weak links to temperature effects.

(e) The more of these abnormal structures are formed at low conversion

the higher will the rate of d [HCl] /dt at high conversions be. This is because at high conversions one gets the accumulative effect of both unstable polymers formed at low conversion which could propagate their weakness with conversion in addition to any other new weaknesses formed during higher conversion due to branching or chain transfer reactions.

(f) Polymers prepared in solution do not follow the same pattern.

(g) In photopolymerisation the trough effect is not obtained probably due to the photo dissociation of impurities and also due to the low polymerisation temperature.

(h) The presence of undetected impurities is evident from the fact that vinyl chloride polymerises in the absence of initiator.

PVC prepared in the presence of solvents, has a greatly reduced molecular weight due to chain transfer to solvent reactions and consequently, the effect of the chain end will be of greater importance with regards to thermal stability. The changes which occur in the thermal stability of PVC prepared in different solvents are very interesting. Some solvent have given increased stability over bulk polymerisation. Of special interest are those prepared in the presence of solvents containing halide, ester, especially plasticisers, and ketone groups. Their optical stability was also significant, except for those prepared with DMF which were exceedingly unstable and formed chomophores at an accelerated rate.

The degradation studies performed on films and their change in absorption reveal two different mechanisms. One being predominant at low temperatures, about 80°C, producing long sequence double bonds chain and a second one taking place around 120°C producing short polyene sequences. This would probably also fit or coincide with the two different rates of dehydrochlorination (R^1 and R^2) described in the beginning of this chapter.

The spectra obtained for degradation carried out at about 120°C consist of a series of absorption maxima which diminish in intensity as the wavelength increases beyond 390 mμ. Sondheimer[138] and coworkers obtained four maxima for polyenes of the type $H(CH = CH)_nH$. Of these two bands at the longest wavelengths had the highest extinction coefficients. Naylor and Whiting[139] on the other hand, found five absorption bands for polyenes of the type $CH_3(CH = CH)_nCH_3$. Whichever type of polyene structure is produced when PVC degrades thermally, it is clear that for each molecule formed having n conjugated double bonds there will be several maxima or bands in its absorption spectrum. In degraded PVC, n will presumably have many values. Consequently, the spectrum of degraded PVC will be an integral of the spectra of the various polyenes present, with due allowance for their proportion in the degraded polymer. Thus both the precise wavelengths at which a maximum occurs, and the absorbance at this wavelength will depend not only upon the number of molecules which have n conjugated double bonds, but also upon the number of molecules with $(n \pm 1)$ and possibly those with $(n \pm 2)$ and $(n \pm 3)$ conjugated double bonds. Lewis and Calvin[54] put forward the equation

$$\lambda^2 = kn$$

where λ is the wavelength, n the number of conjugated double bonds and k is a constant. This equation relates the positions of the absorption maxima with the number of conjugated double bonds in the polyene. The highest wavelength at which it is possible to distinguish a discrete maximum in degraded PVC, at above 120°C., is in the region of 475 mμ.

Assuming that this maximum absorption corresponds to the longest or second longest wavelength, then it corresponds to a polyene containing from 12 to 16 double bonds. Similarly the absorption maxima at 458, 440, 416, 395 and 365 mμ correspond to values of n

from 11-13, 9-11, 8-9 and 6-7 respectively. At wavelengths lower than 365 m μ less overlapping of bands occurs, and fine maxima at 280, 315, 330, 345 and 365 m are obtained for values of 4, 5 and 6.

It appears, therefore, that most of the polyene structures formed during degradation have relatively few double bands. Thus there are many more molecules with 2 or 3 double bands than with 4 or 5 double bonds; and there are more with 4 or 5 double bands than with 6-7 double bonds. As the number of double bands increases beyond 7 the number of molecules formed decreases rapidly, and it seems probable that there are few polyene chains containing 30 conjugated double bands. This type of distribution is not what would be expected if PVC degrades by a conventional zipper reaction at high temperatures (above 120°C). For such a reaction, once initiation had taken place, HCl would be expected to peel off along the polymer molecule very rapidly until some termination process occurred. Thus we might expect a maximum absorption corresponding to a particular polyene chain length with perhaps a symmetrical distribution about this chain length. This is in fact, the type of spectrum obtained for PVC degraded at 100°C and below. Consequently low temperature degradation most probably occurs by some form of zipper reaction.

The thermal degradation of PVC at temperatures above 120°C. is more in line with what would be expected if the degradation proceeds by a series of reaction steps in which polyene molecules with n double bonds are formed from the corresponding molecules with (n-1) double bonds. Although there is a greater proportion of polyenes with four or more conjugated double bonds present in the early stages of degradation than would be expected if the 'allylic' chlorides all were of equal reactivity. Still it is reasonable to expect that the reactivity of the 'allylic' chloride increases with the value of n at least for low values of n.

The polyene conjugated sequences remain relatively short even when degradation is continued for long durations. This could be explained if the normal "head to tail" sequence of monomeric units were interrupted every 10 to 20 units by "head to head" or other anomalous structure such as a pendant - CH_2Cl group. If such abnormal structures do occur, then it would remove allyl type activation at that point and hence prevent further removal of HCl.

Even when long polyene sequences are formed, they appear to be removed during further degradation possibly by free radical chlorine atom attack, or by cyclisation to form aromatic structures[36] followed by chain scission.

The second mechanism occurring at temperatures below 100°C is more difficult to explain. One postulation would be the possibility of free radical reactions occurring at low temperatures initiated by either impurities or free radical chain end fragments. Such reactions would preferentially occur at low temperatures, since high temperatures could have a purging effect which would decompose such impurities.

If the above is true then any allylic chloride structures in which the carbon chlorine bond is already weakened by allylic activation might therefore be weakened still further in the presence of the above impurities, with the result that HCl would be very rapidly liberated zipperwise along the polymer chain until an abnormality in the polymer structure removes the allylic chloride structure or the impurities are exhausted or transformed into a more stable species. Another explanation would be the presence of the second mechanism at the same time as the first, however, it is marked by the distribution of the other conjugated double bonds of different various lengths. The mathematical analysis is the same as that for the polymerisation of ethylene oxide[140]. If Dn is the concentration of double bonds of conjugation degree n, its concentration

as a function of time and reaction rate constant is given by the Poisson distribution function

$$D_n = (kt)^{n-1} e^{-kt} / (n-1)$$

Fig. 4-50 [140] shows the relative concentration of the D_ns as dependent on time and degradation rate constant. Thus as the degradation temperature is increased the effect would be one of shifting towards D1 and at below 100°C towards the higher D.

Thus it is evident from this work that there are at least two distinct mechanisms for the thermal degradation of PVC. One mechanism occurring at temperatures above 100°C, and appears to involve a stepwise elimination of HCl along the polymer chain, and although free radicals are probably involved in the reaction, it is not a normal free radical chain reaction. The other mechanism occurs below 100°C and appears to be a zipper type process and is probably initiated by impurities and free radicals.

The relation of molecular weight to rate of dehydrochlorination is somewhat more complex than has been reported. The method by which the molecular weight was made to vary is the key to the relationship as long as a consistent comparison is made. This is further complicated by the nature of the dehydrochlorination/% polymer conversion curve which shows a minima. Table 4.25 shows how the rate of dehydrochlorination is inversely proportional to the molecular weight of the polymer which conversion corresponds to the minima of the dehydrochlorination rate. The molecular weight was varied by varying the polymerisation temperatures. The initiator used was Bz_2O_2 0.01 M%.

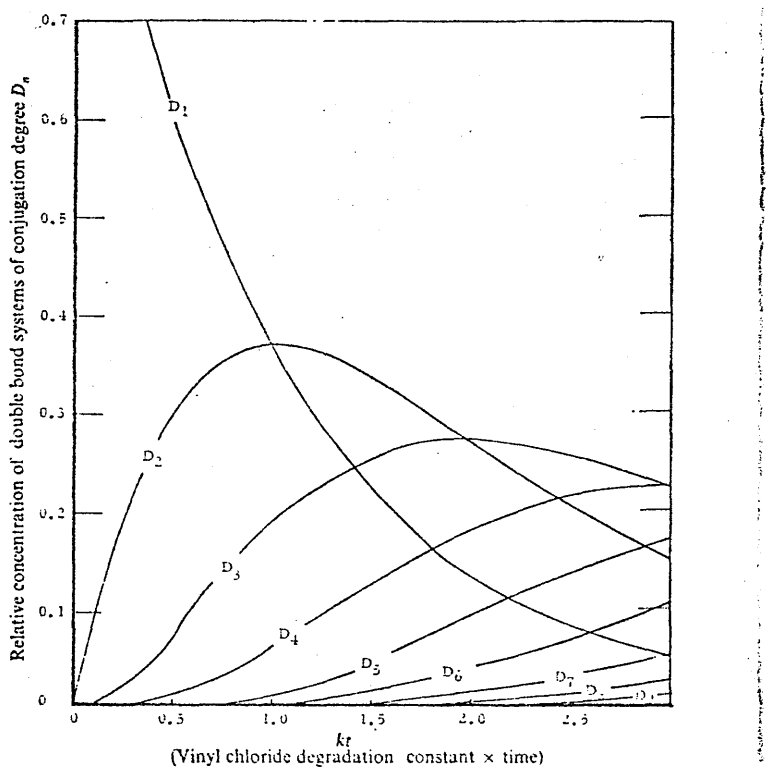


Fig. 4-50 THEORETICAL DISTRIBUTION OF CONJUGATION DEGREE IN HYPOTHETICAL POLY(VINYL CHLORIDE) WITH AN INITIAL SINGLE DOUBLE BOND AT ONE END OF EACH MOLECULE.

Table 4.25. Effect of Molecular Weight on The Dehydrochlorination Rate

Polymerisation Temperature °C.	% Conversion	Average $d\,HCl/dt$ Moles $l^{-1}s^{-1}g^{-1} \times 10^{7}$	$[\eta]$	$\bar{M}n \times 10^{3}$
25	38	0.07	2.40	-
40	43	0.13	1.43	124
60	38	0.38	0.75	70
80	36	1.09	0.43	30

The above will be affected by a certain degree of crystallinity. However, similar results are obtained for polymers of different conversions polymerised at the same temperature except for the conversion at the dehydrochlorination minima. The above would indicate a relationship between the loss of HCl and the polymer chain ends concentration.

The ends of the molecule attached to the initiator fragments are a possibility. The inconclusive results obtained through tracer studies indicate the fast disappearance of such fragments at the very early stages of degradation. The tracer studies also showed the relation between the increasing number of such fragments and the decrease in the stability of the resulting polymer.

Talamini and coworkers have reported[40] that the rate of dehydrochlorination is dependent on the molecular weight of the polymer, but they have also reported[141] that it is independent of this quantity. It is difficult to explain their results, as the polymers used were prepared in several ways at both low and normal temperatures, but the rate appears to be quite independent of the mode of formation of the polymer.

The overall activation energy for dehydrochlorination of commercial suspension PVC was found to be about 21 k cal./mole which is

comparable to the published value of 22 k cal/mole[44]. The activation energy varied depending on the temperature of polymerisation and % conversion.

The activation energy for polyene formation gave two values, indicating two different reactions occurring at different temperatures.

The figure of 22 k cal/mole is surprisingly close to the value of 22.5 k cal/mole reported by Baum and Wartman for 4 - chloro-2-hexene. This provides further evidence for allylic activation of the C-Cl bond.

To conclude, there is considerable evidence to support the view that dehydrochlorination proceeds via allyl type activation, and results in the formation of conjugated polyene structures. Impurities play a major role in the initiation of degradation, initiator fragments at the early stages of degradation and branching at the later stages. The conditions under which the polymer is prepared, predetermines its stability. At least two mechanisms of degradation do occur and one of them can occur at temperatures as low as 80°C.

FUTURE WORK

As would be anticipated from the undertaking of such a study as the one just reported in this thesis, a number of new trends manifest themselves which, in turn, call for further investigation and clarification.

These new approaches could further contribute towards the enhancement of the understanding of the different phenomena involved in the degradation of PVC.

One of the questions which has not been categorically answered is the role of each of the three postulated sites for the initiation of the degradation reaction, i.e. catalyst end fragments, terminal double bonds and thirdly, tertiary chlorine atoms.

The use of tracer techniques with different initiators as well as solvents could provide some answers to the effect of end groups.

Another area of interest is the indication of the existence of two different polyene formation mechanisms. One for high and the other for low temperature degradation. Further studies on low temperature degradation, around 100°C, could thus be useful in defining the initiation of degradation. This could be accompanied with the use of labelled initiators and followed by measuring the quenching effect rather than the actual radioactivity of the degraded polymer. This could provide a more sensitive means of detecting the very early stages of degradation.

Polymers formed at high temperatures, above 90°C, manifested inherent instability. It could prove interesting to polymerise at high temperatures 90, 100 and 110°C then isolate and identify the polymers and use them as degraded polymeric models by studying their rate of

dehydrochlorination by themselves as well as in mixtures of stable polymers and also use them as dead polymer in the preparation of other PVC polymers.

The maxima stability effect with conversion and the two different rates of dehydrochlorination could be further investigated. This could be accomplished by studying the stability of mixtures of different known conversion polymers as well as mixtures of degraded and undegraded polymers.

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